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THE SIMULTANEOUS VOLUMETRIC DETERMINATION OF ZINC AND MAGNESIUM USING DISODIUM DIHYDROGEN ETHYLENEDIAMINE TETRA-ACETATE. I. THE USE OF SELECTIVE pH CONTROL

by

E. G. BROWN AND T. J. HAYES

Research & Development Dept., British Enka Limited, Liverpool (England)

The widely accepted use of disodium dihydrogen ethylenediamine tetra-acetate (complexone III) as a reagent for the volumetric determination of calcium and magnesium[1,2] and the wider application of complexometric procedures to other metals seemed to offer a basis for the determination of zinc and magnesium in admixture. Procedures for the complexometric determination of zinc on the macro[3] and micro[4] scale have been described. PŘIBIL, KOUDELA AND MATYSKA[5] determine zinc by adding excess complexone III followed by back-titration with iron(III) solution. Zinc has also been titrated successfully using an amperometric procedure[6]. SCHWARZENBACH[6] has summarised the general applications of complexometric procedures and mentions the use of Eriochrome black dyes as indicators for magnesium and zinc. To differentiate between the two metal ions using such procedures would apparently require the use either of specific metal ion indicators or the masking of one of the constituents. SCHWARZENBACH[6] cites the use of cyanide and sulphide to mask heavy metals in the titration of alkaline earths. Sodium diethyldithiocarbamate and sodium cyanide have been recommended by DIEHL, GOETZ AND HACH[7] and by BETZ AND NOLL[2]. CHENG, KURTZ AND BRAY[8] also used potassium cyanide in the analysis of limestone. UENO[9] determined zinc by complexometric titration and allowed for traces of magnesium present by titration after precipitation of zinc as zinc sulphide.

Procedures other than complexometric which we examined for the simultaneous volumetric determination of zinc and magnesium included various alkalimetric[10,11,12] titrations. KOLTHOFF[13] refers to his earlier findings[14] on the alkalimetric determination of zinc more especially with reference to the interference of sulphate. These procedures are accurate for pure zinc solutions but in admixture with magnesium it was found that interference occurs, presumably by co-precipitation. Attention was thus centred on the application of a complexometric procedure for the simultaneous determination of zinc and magnesium.

PRELIMINARY INVESTIGATIONS

In the method of UENO[9] the precipitate of zinc sulphide was found to hinder the judgement of end-points. It was therefore thought desirable to evaluate a simpler method which would involve neither the use of cyanide nor a titration in the presence of a precipitate. Observations upon the reactivity of Solochrome Black W.D.F.A. (I.C.I. equivalent of Eriochrome Black T) at various pH values showed that this dyestuff formed a stable complex with zinc ions at a lower pH than with magnesium ions. This selective combination was used to develop a differential complexometric procedure. At a pH of 6.3 the Solochrome indicator becomes pale red in colour and ceases to function as a metal ion indicator. This behaviour has also been noted by BANKS[15]. It was further found that at pH values between 6.3 and 7.0 zinc ions react with the indicator whilst magnesium, in the presence of a maleate buffer solution, only reacts to an appreciable extent in the region of 7.5. A pH of 6.8 was chosen as optimum for the titration of zinc in the presence of magnesium. Of the various buffers used to attain this pH that based upon the di- and mono-sodium maleate buffer due to SMITS[16] proved the most advantageous. Most of the common buffers in the region of pH 6 to 8 are insufficiently buffered according to KOLTHOFF, as quoted by TOMÍČEK[17]. Only sufficient maleate buffer was used to prevent the pH dropping below the safe minimum of pH 6.3. Excess of buffer would hinder the attainment of the optimum pH of 10 necessary for the subsequent titration of magnesium. Ammonium acetate adjusted to pH 6.8 was found to give an inferior end-point to that obtained using the maleate buffer. Oxalate and citrate buffers were also tried but proved unsatisfactory.

PREPARATION AND STANDARDISATION OF SOLUTIONS

The solution of complexone III was initially standardized against pure calcium carbonate. Experience showed that this did not adequately fulfil the requirements of a primary standard in this investigation and metallic zinc was found to be better suited to this purpose. The 0.05M standard zinc solution was prepared according to the recommendations of THEOBALD AND STERN[18] by which zinc is dissolved in liquid bromine. The complexone III solution was prepared using distilled water redistilled in an all Pyrex glass still. This quality of water was used throughout this investigation. The use of highly purified water has been stressed by FLASCHKA[4]. The complexone III solution had a pH below 5; this markedly increases stability, according to GOETZ, LOOMIS AND DIEHL[19]. The Solochrome indicator solution was prepared in a mixture of equal volumes of triethanolamine and *iso*propanol. DISKANT[20] after an examination of various solvents for the Solochrome indicator, proposed the use of diethanolamine or triethanolamine. Unfortunately diethanolamine is a solid at ordinary temperatures in England whilst triethanolamine is a highly viscous liquid. As BETZ AND NOLL had already found that solutions in *iso*propanol were very stable this alcohol was used to dilute the triethanolamine to a reasonable fluidity. This indicator solution in stable for at least a month but a prolonged investigation of its keeping powers has not yet been made.

METHOD

Reagents

0.05*M* *standard zinc solution*[18] — dissolve 3.2690 g of cleaned AnalaR zinc in small quantities of AnalaR bromine and water. When dissolution is complete add 1 ml AnalaR grade hydrochloric acid and expel the excess bromine. Cool and dilute to 1 litre in a volumetric flask. Dilute to a 0.01*M* solution as required.
0.01*M* *Complexone III solution* — dissolve 3.75 g of B.D.H. Laboratory reagent disodium dihydrogen ethylenediamine tetra-acetate in water and make up to 1 litre. Standardize against suitably diluted aliquots of standard zinc solution.
0.025*M* *Magnesium sulphate solution* — dissolve 6.09 g of AnalaR magnesium sulphate $MgSO_4.7H_2O$ in water and make up to 1 litre. Standardize against the 0.01*M* complexone III solution. Dilute to a 0.01*M* solution as required.
Solochrome Black W.D.F.A. indicator — 1 per cent. w/v in a mixture of equal volumes of the purest available triethanolamine and *iso*propanol.
Maleate buffer solution — dissolve 1.218 g of B.D.H. maleic acid in 50 ml of water. Add 20 ml *N* sodium hydroxide solution. Dilute to 100 ml with water in a volumetric flask.
Ammonia-ammonium chloride buffer solution — dissolve 67.5 g of AnalaR ammonium chloride in 570 ml of AnalaR ammonium hydroxide (Sp.Gr. 0.880). Dilute to 1 litre with water.

Procedure

Take an aliquot of solution approximately 0.01*M* with respect to zinc. Neutralise any free acidity by careful addition of an equivalent amount of alkali, as determined upon a separate aliquot, but without adding any acid-base indicator. Add 10 ml of maleate buffer solution for each estimated 25 ml of 0.01*M* zinc solution. Add three drops of Solochrome indicator and titrate to the sharp change from wine-red to blue-grey. If magnesium is now to be titrated, add 2 ml of the ammonia-ammonium chloride buffer solution and titrate to the change from red to pure blue.

RESULTS

The results of the application of the above method to solutions containing various molecular ratios of zinc to magnesium are shown in Table I. The extreme ratios for each element are 3 : 1.

References p. 5.

TABLE I

THE COMPLEXOMETRIC TITRATION OF ZINC AT pH 6.8 AND MAGNESIUM AT pH 10

mg Zn present	mg Zn found	mg Mg present	mg Mg found
25.05	25.02	3.07	3.08
	25.05		3.07
	25.02		3.08
16.70	16.68	6.14	6.15
	16.70		6.14
	16.68		6.14
16.70	16.67	3.07	3.08
	16.67		3.07
	16.68		3.07
8.35	8.35	9.21	9.22
	8.34		9.20
	8.34		9.20
8.35	8.33	6.14	6.14
	8.34		6.14
	8.35		6.14

DISCUSSION

The methods described, as with most procedures involving complexone III, are not specific. We had occasion to apply the above procedure in the presence of traces of iron, lead and calcium. Of these elements iron causes the most trouble. At the pH chosen for the zinc titration iron(II) reacts with the indicator to yield a stable orange-red complex which prevents any colour change occurring. This difficulty was overcome by titration with complexone III at a pH of 2 – 3[8] after oxidation to iron(III), using ammonium thiocyanate, or salicylic acid as indicator. When very small amounts of iron are present zinc hinders the complexing action. Warming to 50° C overcomes this difficulty. The complexed iron(III) caused no further interference. Lead forms a stable complex and titrates with zinc at the lower pH, whilst calcium titrates at higher pH with magnesium. Neutralisation of any free acidity using an internal acid-base indicator on the same aliquot as used for the zinc and magnesium determination decreases the sensitivity of the Solochrome Black end-point. The zinc end-point is deeper than the pure blue of the magnesium end-point.

The proposed procedure has proved to be accurate and simple in manipulation and is suitable for use as a routine method.

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The authors wish to thank the Directors of British Enka Limited for permission to publish these results.

References p. 5.

SUMMARY

The simultaneous volumetric determination of zinc and magnesium using disodium dihydrogen ethylenediamine tetra-acetate (complexone III) is detailed. Selective control of the pH at 6.8 enables zinc alone to be titrated, whilst magnesium is subsequently titrated at pH 10 on the same solution. Solochrome Black is used as indicator for both titrations.

RÉSUMÉ

Les auteurs proposent une méthode volumétrique pour le dosage simultané du zinc et du magnésium au moyen de dihydrogéno-éthylènediamino-tétracétate de sodium (complexon III). Au pH 6.8 le zinc seul peut être titré. La solution est portée ensuite au pH 10 pour la titration du magnésium. Le noir solochrome est utilisé comme indicateur lors de ces 2 titrations.

ZUSAMMENFASSUNG

Die gleichzeitige volumetrische Bestimmung von Zink und Magnesium unter Benützung von Dinatriumdihydrogen-äthylendiamintetra-acetat (Complexon III) wird eingehend beschrieben. Selektive Kontrolle des pH bei 6.8 macht es möglich Zink allein zu titrieren, während Magnesium darauffolgend bei pH 10 in der gleichen Lösung titriert wird. Solochromschwarz wird als Indikator für beide Titrationen benützt.

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THE SIMULTANEOUS VOLUMETRIC DETERMINATION OF ZINC AND MAGNESIUM USING DISODIUM DIHYDROGEN ETHYLENEDIAMINE TETRA-ACETATE. II. THE USE OF THE ZINC, FERROCYANIDE, FERRICYANIDE REDOX SYSTEM

by

E. G. BROWN AND T. J. HAYES

Research & Development Dept., British Enka Limited, Liverpool (England)

The procedure for the volumetric determination of zinc by precipitation of the insoluble potassium zinc ferrocyanide in neutral or acid medium has been in general use for many years. The correct conditions for this method were evaluated by KOLTHOFF AND PEARSON[1] who recommended back-titration as the more accurate technique. The method requires strict control of conditions.

BELCHER AND NUTTEN have recommended the use of naphthidine[2] (4:4'-diamino 1:1'-dinaphthyl) and 3:3'-dimethyl naphthidine[3] (3:3'-dimethyl 4:4'-diamino 1:1'-dinaphthyl) as internal indicators for this titration. When 3:3'-dimethyl naphthidine is added to an acid solution of zinc containing ferricyanide the indicator is oxidised to a deep red-violet[4]. On titrating, addition of the slightest excess of ferrocyanide causes a reduction in the potential and the indicator becomes pale grey-green.

PRELIMINARY INVESTIGATIONS

It seemed feasible that a similar change in potential as in the ferrocyanide titration procedure could be brought about by removing zinc ions from solution as the complex cation formed with complexone III. This was justified experimentally. At the start of the titration the indicator is in the oxidised form. Removal of active zinc ions causes a drop in potential at the end-point and the red-violet colour disappears. The solution was buffered at pH 5, using a sodium acetate, hydrochloric acid buffer. The change was somewhat slow and near the end-point it was necessary to allow 10 to 15 seconds between successive additions of complexone, the solution being swirled vigorously. After titration of the zinc the pH of the solution was raised to 10 by adding an ammonia-ammonium chloride buffer. The magnesium was then titrated with complexone III using Solochrome W.D.F.A. as indicator. This forms a wine red, slightly dissociated complex with magnesium which reverts to pure blue on extraction of the magnesium by the complexing titrant. The presence of ferricyanide somewhat alters the colour of the end-point from that obtained in pure solutions of magnesium, giving it a slight green cast. It should be noted that the potassium ferricyanide used in our proposed procedure should contain traces of ferrocyanide, otherwise preliminary oxidation of the dimethyl naphthidine indicator will not occur. AnalaR potassium ferricyanide contains about 0.005% of ferrocyanide.

METHOD

Reagents. The following reagents are needed in addition to those used in Part I of these investigations.

Potassium ferricyanide. 1 per cent. w/v aqueous solution of AnalaR potassium ferricyanide. Prepare fresh daily.

3:3'-dimethyl naphthidine. 1 per cent. w/v solution in AnalaR glacial acetic acid. The solid indicator may be prepared according to the method of FRIES AND LOHMANN[5].

Sodium acetate — hydrochloric acid buffer. Dilute a solution containing 27.22 g AnalaR sodium acetate trihydrate and 60 ml *N*-hydrochloric acid to one litre with water.

Procedure

To a neutral 25 ml aliquot of the zinc solution, approximately 0.01*M* with respect to zinc, add 10 ml of sodium acetate — hydrochloric acid buffer solution. Add 1 micro-drop of potassium ferricyanide solution from a capillary and 3-4 micro-drops of 3:3'-dimethyl naphthidine. A violet-red colour will develop. Titrate slowly with 0.01*M* complexone III solution until the indicator begins to fade. Continue the titration allowing 10 to 15 seconds to elapse between additions and swirling the solution vigorously until the last trace of pink has disappeared. If magnesium is now to be titrated, add 2 ml of ammonia-ammonium chloride buffer and 3 drops of Solochrome Black indicator. Titrate till the last trace of red has disappeared and the indicator reverts to a pure blue colour.

RESULTS

The results obtained on titrating 0.01*M* zinc solutions by the proposed procedure are given in Table I and the results obtained in the presence of various molecular ratios of magnesium are shown in Table II.

DISCUSSION

The method as described lacks specificity in common with procedures based upon the use of complexone III. 3:3'-dimethyl naphthidine is sensitive to certain oxidising agents, *e.g.*, vanadate, dichromate, whilst the Solochrome indicator

TABLE I

COMPLEXOMETRIC TITRATION OF Zn^{+2},$[Fe(CN)_6]^{-3}$,$[Fe(CN)_6]^{-4}$ REDOX SYSTEM

Zn^{+2} solution 0.00998*M*
Complexone III solution 0.01004*M*

ml Zn^{+2} solution	ml complexone solution theoretical	ml complexone solution found	mg Zn present	mg Zn found
25.00	24.87	24.90	16.32	16.34
		24.87		16.32
20.00	19.90	19.90	13.05	13.05
		19.91		13.06
10.00	9.95	9.96	6.53	6.54
		9.95		6.53
5.00	4.97	4.98	3.26	3.27
		4.97		3.26

TABLE II

COMPLEXOMETRIC TITRATION OF Zn^{+2} AND Mg^{+2} TOGETHER

Zn^{+2} solution 0.00998*M*
Complexone III solution 0.01004*M*

ml Zn^{+2} solution	ml complexone solution theoretical	ml complexone solution found	mg Zn present	mg Zn found
20.00	19.89	19.85	13.05	13.03
		19.83		13.02
		19.88		13.04
		19.89		13.05
		19.91		13.06
		19.91		13.06

TABLE II (continued)

Mg^{+2} solution 0.00994*M*
Complexone III solution 0.01004*M*

ml Mg^{+2} solution	ml complexone solution theoretical	ml complexone solution found	mg Mg present	mg Mg found
40.00	39.81	39.68	9.72	9.69
		39.70		9.69
25.00	24.76	24.82	6.04	6.06
		24.79		6.05
10.00	9.90	9.93	2.42	2.42
		9.93		2.42

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reacts with many ions to yield coloured complexes. These metals also react with complexone III. Iron(II) and iron(III) interfere badly by formation of coloured precipitates and considerably modify the indicator end-point. This method is regarded as inferior to that detailed in Paper I, mainly because of the slowness of the end-point, but does bring to light the possibility of causing a redox change by complexometric procedures. PŘIBIL[6] and co-workers have noted that complexones stabilise higher valency states for certain elements, *e.g.*, cobalt(III) and manganese(III) and utilise the lowering of potential caused by complexing to elaborate oxidimetric[6,7] procedures. The direct use of complexone III to bring about a redox reaction embodies a somewhat different principle which may be of some value as applied to other systems.

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SUMMARY

The simultaneous volumetric determination of zinc and magnesium using disodium dihydrogen ethylenediamine tetra-acetate (complexone III) is described. Complexone III removes zinc ions from the redox system zinc, ferrocyanide, ferricyanide, causing a reduction in potential at the end-point which is marked by a suitable indicator, 3:3′-dimethyl naphthidine. Magnesium is then titrated with complexone III in the same solution using Solochrome Black as indicator.

RÉSUMÉ

Un dosage volumétrique simultané pour le zinc et le magnésium, au moyen de dihydrogéno-éthylènediamino-tétracétate disodique (complexon III), est décrit. Le complexon (III) masque les ions Zn^{+2} dans le système rédox zinc, ferrocyanure, ferricyanure, causant une diminution de potentiel. La fin de la titration est déterminée à l'aide d'un indicateur: la 3:3′-diméthylnaphtidine. Le magnésium est ensuite titré à l'aide de complexon (III) dans la même solution en utilisant le noir solochrome comme indicateur.

ZUSAMMENFASSUNG

Die gleichzeitige volumetrische Bestimmung von Zink und Magnesium mit Dinatriumhydrogen-äthylendiamintetra-acetat (Complexon III) wird beschrieben. Complexon III entfernt die Zinkionen aus dem Redoxsystem Zink, Ferrocyanid, Ferricyanid, indem es eine Potentialerniedrigung am Endpunkt verursacht, der durch einen geeigneten Indikator, dem 3:3′-Dimethylnaphthidin bestimmt wird. Magnesium wird dann mit Complexon III mit Solochromschwarz als Indikator in der gleichen Lösung titriert.

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A MICROVOLUMETRIC DETERMINATION OF TIN IN TIN-BASE AND LEAD-BASE ALLOYS

by

CH. CIMERMAN AND M. ARIEL

Laboratory of Analytical Chemistry and Microchemistry, Hebrew Institute of Technology, Haifa (Israel)

INTRODUCTION

In 1931, HÖLTJE[1] elaborated a microvolumetric method for the determination of small quantities of tin (0.3-1 mg). His method was based on the reduction of tin with iron powder (ferrum reductum), and its subsequent titration with $0.01N$ iodine solution. The precision of the results obtained by this method, as given by MIKA[1], was ±0.005 mg, giving a relative error of ±0.5% for 1 mg of tin. The method had not been applied to alloys.

In 1948, MILLER AND CURRIE[2] evolved another volumetric method for the determination of 0.1-1 mg tin, based on the reduction of tin with freshly cast antimony, and subsequent titration with $0.1N$ iodine solution, measured from a special microburette of 0.2 ml capacity. Excess of iodine solution was back-titrated with $0.001N$ sodium thiosulphate solution. The authors applied this method to the determination of tin in various alloys; the precision of results for lead-base and tin-base alloys, as given in their publication, is variable — side by side with very exact results, some varying from —1.3% to +0.9% (relative error) were reported.

While searching for a rapid and exact method for the micro-determination of tin, with a view to applying it to the analysis of tin-base and lead-base alloys, we have chosen HÖLTJE's method, which appeared simpler than that of MILLER AND CURRIE.

Our object was to check this method on pure tin, and later attempt to extend its application to the a.m. alloys, keeping in mind EVANS AND HIGGS'[3] remark that iron is not suitable as reductant for tin in alloys, as the antimony and copper precipitated during reduction tend to carry down some of the tin.

Our attempts to apply HÖLTJE's method to the analysis of pure tin constantly gave high results: this was probably due to the presence of some undissolved iron at the end of the reduction period, which subsequently reduced some of the Sn(IV) formed during the titration.

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Table I shows some of the results obtained by HÖLTJE's method.

TABLE I

DETERMINATION OF TIN ACCORDING TO HÖLTJE'S METHOD

Exp. No.	Sn present mg	Sn found mg	Difference mg	Relative Error %
1	0.500	0.517	+0.017	+3.4
2	1.000	1.023	+0.023	+2.3
3	2.000	2.025	+0.025	+1.2
4	2.500	2.577	+0.077	+3.1

HÖLTJE's method not having given us satisfactory results, we decided to attempt the further study of the micro-determination of tin, with a view to evolving an exact method, using iron powder, reduced by hydrogen, as reductant, and a solution of potassium iodate-iodide 0.01*N* or 0.02*N* as titrant.

EXPERIMENTAL

Reagents and standard solutions

The reagents employed were:

1. Tin solution I (0.2500 g tin dissolved in 10 ml conc. hydrochloric acid, oxidised with perhydrol, and made up to 1 litre).
2. Tin solution II (1.0000 g tin dissolved in 25 ml conc. hydrochloric acid, oxidised with perhydrol, and made up to 1 litre).
3. Conc. hydrochloric acid.
4. Iron powder reduced by hydrogen.
5. Potassium iodide.
6. Standard 0.01*N* potassium iodate-iodide solution (prepared by dissolving 0.3567 g KIO_3 in 200 ml H_2O containing 1 g NaOH and 2-3 g KI, and making up to 1 litre).
7. Standard 0.02*N* potassium iodate-iodide solution (prepared by dissolving 0.7134 g KIO_3 in 200 ml H_2O containing 1 g NaOH and 2-3 g KI, and making up to 1 litre).
8. 1% starch solution.
9. Carbon dioxide gas from a Kipp's apparatus, bubbled through a conc. solution of sodium bicarbonate.
10. Bi-distilled water for the preparation of all the a.m. solutions, and all operations described in the following pages.

Procedure employed for the elaboration of the method

(Following HÖLTJE'S method, as given by MIKA[1])

2.5 ml of tin solution II were introduced into the reduction vessel, 0.1 g iron powder and 10-20 mg potassium iodide (for facilitating reduction) added, a stream of carbon dioxide passed incessantly through the solution*, and the vessel heated in a boiling water bath. Additional iron powder and hydrochloric acid were added at the fixed intervals recommended in the method, and heating continued until all the iron dissolved. The vessel was removed from the water bath, cooled, the solution diluted with air-free bi-distilled water to approx. 15 ml, and titrated with $0.01N$ potassium iodate-iodide solution, using 0.1 ml of a 1% starch solution as indicator, to the first discernible blue colour.

Remark

Preliminary experiments indicated that the choice of the proper vessel for reduction was of the utmost importance; accordingly, vessels of various shape and capacity were tested, with a view to picking the vessel best suited to this purpose.

Table II illustrates some of the results obtained.

TABLE II

INFLUENCE OF SHAPE OF REDUCTION VESSEL ON RESULTS

Exp. No.	Reduction Vessel	Sn present mg	Sn found mg	Difference mg	Relative Error %
1	Test tube (pyrex glass) 18 mm diameter 150 mm height	2.500	2.558	+0.058	+2.3
2		,,	2.597	+0.097	+3.9
3		,,	2.606	+0.106	+4.2
4	Erlenmeyer flask (pyrex glass) 25 ml cap.	,,	2.480	−0.020	−0.8
5		,,	2.463	−0.037	−1.5
6		,,	2.421	−0.079	−3.2
7	Kjeldahl flask (pyrex glass) 30 ml cap.	,,	2.504	+0.004	+0.2
8		,,	2.511	+0.011	+0.4
9		,,	2.508	+0.008	+0.3

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* This stream of carbon dioxide is kept up throughout the determination, until the end of the titration.

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DISCUSSION

1. Results obtained with test tube (18 mm × 150 mm) were too high (Exp. 1-3). This was due, probably, to the incomplete solution of the iron powder, as was the case in our attempts to use the reduction vessel recommended by Mika[1] (a cylindrical, flat-bottomed vessel, measuring 14 mm × 130 mm).

2. Substitution of an Erlenmeyer flask of 25 ml capacity greatly accelerated solution of the iron, its shape permitting more efficient stirring of the solution. On the other hand, the far greater surface of the solution allowed the oxidation of some of the Sn(II) by air, thus causing low results. Some loss may also result from ejection. (Exp. 4-6).

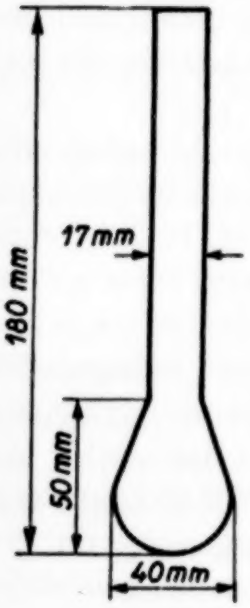

Fig. 1. Kjeldahl flask, 30 ml details of construction.

3. A Kjeldahl flask of 30 ml capacity combines the positive qualities of the a.m. vessels: its rounded lower part facilitates efficient solution of the iron, while its long neck prevents losses due to ejection and, filled with carbon dioxide, provides adequate protection against air oxidation. (Exp. 7-9). This flask was therefore chosen as most suitable for the reduction of tin, and was used in all subsequent experiments. Fig. 1 gives the exact measurements of the flask used.

Once the Kjeldahl flask had been picked as reduction vessel, efforts were made to shorten the time necessary for reduction of the tin and for the complete solution of the iron. This was achieved by introducing all of the iron powder at the beginning of the reduction (and not by instalments during the reduction), and by using conc. acid instead of 3 HCl : 2 H_2O acid used by Höltje. Reduction was practically complete after 30-40 minutes, as compared with at least 1 hour by Höltje's method.

Table III indicates some of the results obtained under the conditions described above.

TABLE III

TITRATION OF TIN; ALL THE IRON POWDER ADDED AT THE START; CONC. HYDROCHLORIC ACID USED; REDUCTION PERIOD 30-40 MINUTES

Exp. No.	Sn present mg	Sn found mg	Difference mg	Relative error %
1	5.000	4.988	−0.012	−0.2
2	2.500	2.494	−0.006	−0.2
3	1.000	0.997	−0.003	−0.3

CONCLUSION

As indicated by Table III, results are exact (maximum relative error: — 0.3%).

Based on the above results, the following method is recommended for the determination of tin in tin metal:

PROCEDURE

1-5 mg of tin in 4-8 ml of a slightly hydrochloric acid solution are introduced into a Kjeldahl flask of 30 ml capacity (Fig. 1), approx. 0.3 g iron powder reduced by hydrogen, approx. 10 mg potassium iodide and 2 ml conc. hydrochloric acid added, the neck of the flask rinsed with bi-distilled water, and the volume of the liquid in the flask made up to approx. 15 ml. A long capillary is introduced into the solution and a brisk stream of carbon dioxide (purified by passing through a conc. solution of sodium bicarbonate) bubbled through it*.

The flask is heated in a boiling water bath for 30 minutes; should appreciable iron powder be left after 25 minutes, an additional ½-1 ml conc. hydrochloric acid is added and heating continued until all the iron is dissolved. If the volume has decreased appreciably through evaporation, it is made up with some air-free bi-distilled water. The flask is removed from the water bath, cooled on ice, 0.1 ml of 1% starch solution added and the tin titrated with potassium iodate-iodide standard solution (measured from a microburette of 5 ml capacity, graduated to 1/100 ml, and delivering about 100 drops per ml), to the first discernible blue colour. Rinsing of the sides of the flask is conveniently effected by temporarily increasing the flow of carbon dioxide. For samples containing 1-3.5 mg tin, $0.01N$ potassium iodate-iodide standard solution was used; for samples containing 3.5-5 mg tin, $0.02N$ solution was preferred.

Time required for 1 determination: 50-60 minutes.

CALCULATION OF RESULTS

1 ml $0.01N$ KIO_3-KI solution ⟶ 0.5935 mg tin
1 ml $0.02N$ KIO_3-KI solution ⟶ 1.187 mg tin.

APPLICATION OF THE METHOD FOR THE DETERMINATION OF PURE TIN TO TIN-BASE ALLOYS

Once the method for pure tin had been established, it was attempted to apply it to the determination of tin in U.S.A. National Bureau of Standards Alloy No. 54c. This is a Tin-Base Bearing Metal, containing:

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* This stream of carbon dioxide is kept up throughout the determination, until the end of the titration.

References p. 21.

86.29% tin, 7.28% antimony, 1.99% lead, 4.30% copper, 0.033% iron, 0.028% bismuth, 0.012% nickel, 0.049% arsenic, and 0.02% silver. For this purpose, aliquots of a hydrochloric solution, containing 1 g of the alloy per litre, were used.

Table IV shows some of the results obtained.

TABLE IV

DETERMINATION OF TIN IN ALLOY NO. 54C, USING THE UNMODIFIED METHOD FOR PURE TIN

Exp. No.	Alloy No. 54c mg	Sn present mg	Sn found mg	Difference mg	Reduction period hours	Total HCl added ml	Relative error %
1	5.000	4.314	4.384	+0.070	½	2	+1.6
2	,,	,,	4.398	+0.084	½	3	+1.9
3	,,	,,	4.328	+0.014	1¾	2	+0.3
4	,,	,,	4.328	+0.014	1¾	3	+0.3

CONCLUSION

As indicated by Table IV, for reduction periods of 30 minutes, results are too high. For longer reduction periods, improved results were obtained; these, however, may be due to compensation of high results by losses through the oxidation of some of the Sn(II) by air. The method established for pure tin, cannot — such as it is — be applied to tin-base alloys.

DISCUSSION

1. It was observed during the attempted analysis of alloy No. 54c, that the iron powder used for reduction dissolved extremely slowly, and, even after 1½ hours' heating in the boiling water bath, some of it probably remained undissolved.
2. Antimony precipitated during the reduction made it impossible to ascertain whether all of the iron finally dissolved.
3. Increase of acidity through the addition of conc. hydrochloric acid did not appreciably accelerate solution of the iron.
4. The fact that certain types of iron, under certain reaction conditions, show a tendency towards passivity[4] may play a part in the difficulties encountered in the solution of the iron.

The unmodified method having proved unapplicable, it was decided to attempt partial precipitation of antimony with iron in acid medium, and its removal by filtration prior to the reduction of the tin. An aliquot of the above alloy solution was introduced into a micro beaker of pyrex glass (18 mm diameter, 55 mm height), and 0.3-0.4 g iron powder added carefully. After 2-3 minutes, the solution was filtered through a glass filterstick (overall diameter 11 mm, outside stem diameter 3.5 mm, inside stem diameter 2 mm, overall height 110 mm) into a Kjeldahl flask of 30 ml capacity (Fig. 2), and the beaker rinsed with 6-8 portions of 1.0 ml of 1:4 hydrochloric acid. The contents of the flask were later treated as in the procedure for pure tin, merely omitting the addition of 2 ml hydrochloric acid, as sufficient acid had been introduced through the rinsing. After 25 minutes of heating, 1-2 ml of conc. hydrochloric acid were added.

Some of the results obtained are given in Table V.

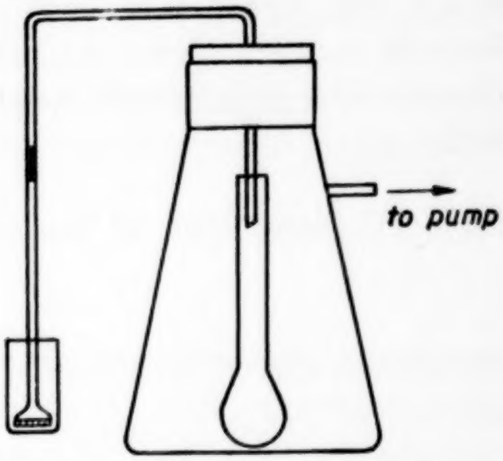

Fig. 2. Apparatus for filtration.

TABLE V

DETERMINATION OF TIN IN ALLOY NO. 54C AFTER PARTIAL REMOVAL OF ANTIMONY

Exp. No.	Alloy No. 54c mg	Sn present mg	Sn found mg	Difference mg	Relative error %
1	5.000	4.314	4.328	+0.014	+0.3
2	2.000	1.726	1.733	+0.007	+0.4
3	1.000	0.863	0.862	—0.001	—0.1

CONCLUSION

As indicated by Table V, results are exact (maximum relative error ±0.4%).

The following method is, therefore, recommended for the determination of tin in tin-base alloys:

PROCEDURE

A sample containing 1-5 mg tin is introduced into a micro beaker of pyrex glass (18 mm diameter, 55 mm height) and dissolved by warming gently with 1 ml conc. hydrochloric acid and 1-2 drops of perhydrol. During the solution, the beaker is covered with a small watch glass. When the alloy has dissolved completely, watch glass and sides of beaker are rinsed with about 1 ml of bi-distilled water, and the solution cooled. 0.3-0.4 g of iron powder are carefully added, and, after 2-3 minutes, the solution is filtered into a Kjeldahl flask of 30 ml capacity (Fig. 1) by means of a glass filterstick (Fig. 2). The beaker and the filterstick are rinsed with 6-8 portions of 1.0 ml of 1:4 hydrochloric acid. The volume of the solution is made up to approx. 15 ml with bi-distilled water, approx. 0.3 g iron powder and approx. 10 mg potassium iodide are added to the flask, a brisk stream of carbon dioxide (purified by passing through a conc. solution of sodium bicarbonate) bubbled through the solution, and the flask heated in a boiling water bath for 30-40 minutes*. Additional hydrochloric acid (1-2 ml) may be added if, after 30 minutes heating, appreciable iron remains undissolved. If the volume of the solution has decreased due to evaporation, some air-free bi-distilled water is added to make up the volume. After reduction has been completed, the flask is cooled in an ice bath, 0.1 ml of a 1% starch solution added and the tin titrated with standard potassium iodate-iodide solution ($0.01N$ or $0.02N$), measured from a microburette of 5 ml capacity, graduated to 1/100 ml, and delivering about 100 drops per ml, to the first discernible blue colour. Rinsing of the sides of the flask may be effected by temporarily increasing the flow of carbon dioxide.

APPLICATION OF THE METHOD TO THE DETERMINATION OF TIN IN LEAD-BASE ALLOYS

Essentially the same method was next applied to samples of U.S.A. National Bureau of Standards Alloy No. 53c. This is a Lead-Base Bearing Metal, containing: 5.16% tin, 10.20% antimony, 0.214% copper, 0.0017% iron, 0.093% bismuth, 0.0023% nickel, 0.044 arsenic and lead (the rest). The high lead content of this alloy made the removal of the major part of the lead as $PbCl_2$ advisable, as, failing this, the lead appeared as PbI_2 before or during the titration, generally interfering with the determination. The removal of the lead was effected by diluting the solution, after the precipitation of antimony, to a hydrochloric acid content of approx. 1:4, this being the acid concentration at which $PbCl_2$ is least soluble[5], and cooling thoroughly. The solution was next filtered as usual, by means of a glass filterstick (Fig. 2), the beaker and precipitate rinsed with 1:4 hydrochloric acid, and the solution treated as recommended for tin-base alloys.

Table VI shows some of the results obtained under the above conditions.

CONCLUSION

As indicated by Table VI, results are exact (maximum relative error —0.4%).

Based on the above, the following procedure is recommended for the determination of tin in lead-base alloys:

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* This stream of carbon dioxide is passed continuously up to the end of the titration.

References p. 21.

TABLE VI

DETERMINATION OF TIN IN LEAD-BASE ALLOY NO. 53C

Exp. No.	Alloy No. 53c mg	Sn present mg	Sn found mg	Difference mg	Relative error %
1	56.990	2.941	2.934	−0.007	−0.2
2	34.934	1.802	1.795	−0.007	−0.4
3	24.876	1.283	1.281	−0.002	−0.2

PROCEDURE

This is essentially similar to the procedure for tin-base alloys, with some modifications:

A sample containing 1-3 mg* tin is introduced into a micro beaker of pyrex glass (18 mm diameter, 55 mm height) and dissolved by warming gently with 2.5 ml conc. hydrochloric acid to which 2-3 drops of perhydrol have been added; during solution the beaker is covered with a small watch glass. Care must be taken to keep the liquid yellowish; should it turn water clear, another drop of perhydrol is carefully added. The solution is next heated more strongly and concentrated to approx. 1.5 ml. The watch glass and the sides of the beaker are rinsed with about 1.5 ml of bi-distilled water, the solution is cooled and 0.3-0.4 g of iron powder carefully added. After 2-3 minutes, the solution is filtered and washed as recommended in the procedure for tin-base alloys. Most of the $PbCl_2$ is removed in this way. The determination is continued as for tin-base alloys.

It was deemed expedient to test the above methods on a series of alloys with a greatly varying tin content (*e.g.* 15%-70%). Standard alloys being unavailable, varying amounts of pure tin were dissolved simultaneously in the same beaker with varying amounts of alloy No. 53c, and their solutions treated as above. Removal of $PbCl_2$ was carried out on samples with high lead content.

Table VII gives some of the results obtained.

CONCLUSION

As indicated by Table VII, results are exact (maximum relative error + 0.3%).

Both of the alloys No. 54c and No. 53c being low in copper content, it was decided to add standard cupric sulphate solution (30 g $CuSO_4.5H_2O$ per litre)

---

* Use of samples containing more than 3 mg tin, entails an increase of the absolute quantity of antimony in the solution; this was found to have an adverse effect on the analysis. (Compare: General Discussion of Factors Important for the Determination of Tin, point 7).

TABLE VII

DETERMINATION OF TIN IN VARIOUS MIXTURES OF PURE TIN AND ALLOY NO. 53C

Exp.	Pure	Alloy	% Sn	% Sb	% Cu	Sn	Sn	Difference	Relative
No.	Tin	53c	calculated			present	found		error
	mg	mg				mg	mg	mg	%
1	3.820	31.835	15.32	9.11	0.191	5.463	5.461	−0.002	−0.04
2	4.310	26.361	18.49	8.77	0.184	5.670	5.684	+0.014	+0.2
3	4.746	8.977	37.96	6.67	0.140	5.209	5.227	+0.018	+0.3
4	4.548	5.551	47.87	5.60	0.117	4.834	4.844	+0.010	+0.2
5	4.332	2.823	62.59	4.02	0.084	4.478	4.493	+0.015	+0.3
6	5.602	2.454	71.11	3.11	0.065	5.729	5.740	+0.011	+0.2

to solutions of samples of those alloys, in order to test the applicability of the method to alloys having a higher copper content. Enough cupric sulphate solution was added to bring the copper content to about 10%. The usual procedures were adhered to, practically all the copper being precipitated during the preliminary precipitation of antimony. It was found better, however, to wash with some conc. hydrochloric acid at first. As a rule, more antimony was left unprecipitated and consequently complete solution of all the iron powder, after 30-40 minutes of heating, was not always achieved. In spite of that, it was found possible to prevent high results, due to the reducing action of the undissolved iron during the titration, by keeping the reduction flask in the ice bath during the titration and titrating rapidly.

Table VIII shows some of the results obtained.

TABLE VIII

DETERMINATION OF TIN IN ALLOY 54C AND ALLOY 53C WITH ADDITION OF CUPRIC SULPHATE TO A COPPER CONTENT OF APPROX. 10%

Exp. No.	Alloy No. 54c mg	Alloy No. 53c mg	Sn present mg	Sn found mg	Difference mg	Relative error %
1	4.900	—	4.228	4.228	—	—
2	4.751	—	4.100	4.084	−0.016	−0.4
3	6.305	—	5.440	5.417	−0.023	−0.4
4	—	52.157	2.691	2.691	—	—
5	—	44.018	2.271	2.272	+0.001	+0.04
6	—	46.824	2.416	2.412	−0.004	−0.2

References p. 21.

CONCLUSION

As indicated by Table VIII, results are exact (maximum relative error —0.4%).

Based on the above, the following procedure is suggested for alloys containing 3-10% of copper:

PROCEDURE

The sample containing 1-5 mg tin is dissolved as usual, and antimony, lead and copper precipitated and filtered off as recommended for tin-base alloys. The excess iron powder together with the precipitated metals (Sb, Cu) and $PbCl_2$ are washed with 2 portions of 0.5 ml of conc. hydrochloric acid. Subsequent washing and reduction are carried out as for tin-base alloys. In case some of the iron remains undissolved after the usual reduction period, titration is carried out with the flask in an ice bath.

GENERAL DISCUSSION OF FACTORS IMPORTANT TO THE DETERMINATION OF TIN BY THE PROPOSED METHOD

From the experiments outlined above, the following factors were found salient and of considerable influence on the accuracy and speed of the determination:

1. The reduction vessel had to be as simple and as easily available as possible; its shape had to be such as to prevent any losses by ejection (due to the rather violent reaction of the iron powder at the beginning of the reduction, or to the brisk bubbling of carbon dioxide through the mixture); and, most important, it had to provide adequate protection against air oxidation of the reduced tin, allowing, at the same time, the fairly rapid solution of the iron. All these qualities were found in the Kjeldahl flask of 30 ml capacity (Fig. 1).
2. Iron powder reduced by hydrogen may be used as reductant for tin under the conditions described (including tin in alloys of the tin-base and lead-base types, containing Pb, Sb, Cu).
3. Addition of all the iron powder and most of the conc. hydrochloric acid at the beginning of the reduction shortened the reduction period.
4. Reduction periods of 30-40 minutes were found to be most suitable. Shorter periods often resulted in incomplete reduction, while prolonged boiling after all the iron had dissolved occasionally also caused low results, due, probably, to oxidation by air.
5. A brisk stream of carbon dioxide was found necessary to provide a sufficient blanket of gas over the reaction mixture; by stirring the mixture, it also facilitated the solution of the iron powder; this was important where solution of the iron was slowed down, *i.e.* in the analysis of alloys.
6. Proper cooling of the reduced solution before titrating was found to be im-

References p. 21.

portant; where all the iron had dissolved during reduction, it was found sufficient to cool and titrate at about 10° C; but whenever any of the iron remained, it was found advisable to keep the flask in an ice bath during the titration. In all cases, titration should be fairly rapid..

7. The presence of appreciable amounts of antimony gravely hindering the solution of the iron powder used for reduction, a preliminary precipitation with iron powder was carried out to remove a major part of the antimony. Practically all the copper present was removed at the same time. In alloys with a high lead content most of the lead was removed by a method recommended by COHEN[5], which makes use of the dilution of the alloy solution to an acid content of 1:4, at which concentration $PbCl_2$ is least soluble.

8. The iodometric determination of tin is generally counted among the more delicate methods; this is especially so on the micro scale. Strict observation of all conditions, purity of reagents and of apparatus are required, if reliable results are to be obtained.

SUMMARY

The authors have elaborated a rapid and exact microvolumetric method for the determination of tin in metallic tin and in tin-base and lead-base alloys.

RÉSUMÉ

Les auteurs ont élaboré une microméthode volumétrique rapide et exacte pour la détermination de l'étain dans l'étain métallique et dans les alliages à base d'étain et de plomb.

ZUSAMMENFASSUNG

Die Verfasser haben eine schnelle und exakte Mikrovolumetrische Methode zur Bestimmung des Zinns im metallischem Zinn, und in Blei und Zinn Legierungen ausgearbeitet.

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POTASSIUM META-PERIODATE AS VOLUMETRIC REAGENT
V. IODINE BROMIDE METHOD

by

BALWANT SINGH AND APAR SINGH

Panjab University College. Hoshiarpur (India)

Potassium meta-periodate in acid solution is a strong oxidising agent and is reduced to iodine:

$$2\,IO_4^- + 16\,H^+ + 14\,e = I_2 + 8\,H_2O$$

The iodine is further oxidised by the periodate

$$3\,I_2 + IO_4^- + 8\,H^+ = 7\,I^+ + 4\,H_2O$$

Iodine cation forms a stable iodine bromide complex in the presence of a high concentration of bromide ion.

$$I^+ + 2\,Br^- = IBr_2^-$$

This method is, therefore, based on titration in acid medium with potassium meta-periodate in presence of large excess of potassium bromide. The periodate reacts in accordance with the following equations:

$$\begin{array}{l}
3\,I^- + IO_4^- + 8\,H^+ + 8\,Br^- = 4\,IBr_2^- + 4\,H_2O \\
3\,As_2O_3 + 2\,IO_4^- + 4\,H^+ + 4\,Br^- = 3\,As_2O_5 + 2\,IBr_2^- + 2\,H_2O \\
3\,Sb_2O_3 + 2\,IO_4^- + 4\,H^+ + 4\,Br^- = 3\,Sb_2O_5 + 2\,IBr_2^- + 2\,H_2O \\
3\,Sn^{+2} + IO_4^- + 8\,H^+ + 2\,Br^- = 3\,Sn^{+4} + IBr_2^- + 4\,H_2O \\
3\,Hg_2^{+2} + IO_4^- + 8\,H^+ + 2\,Br^- = 6\,Hg^{+2} + IBr_2^- + 4\,H_2O \\
3\,SO_3^{-2} + IO_4^- + 2\,H^+ + 2\,Br^- = 3\,SO_4^{-2} + IBr_2^- + H_2O \\
3\,S_2O_3^{-2} + 4\,IO_4^- + 2\,H^+ + 8\,Br^- = 6\,SO_4^{-2} + 4\,IBr_2^- + H_2O \\
3\,S_4O_6^{-2} + 7\,IO_4^- + 14\,Br^- + 2\,H_2O = 12\,SO_4^{-2} + 4\,H^+ + 7\,IBr_2^- \\
6\,Fe^{+2} + IO_4^- + 8\,H^+ + 2\,Br^- = 6\,Fe^{+3} + IBr_2^- + 4\,H_2O \\
CNS^- + IO_4^- + 2\,Br^- = SO_4^{-2} + IBr_2^- + CN^- \\
3\,N_2H_4 + 2\,IO_4^- + 4\,H^+ + 4\,Br^- = 3\,N_2 + 2\,IBr_2^- + 8\,H_2O \\
3\,C_6H_5NH.NH_2.HCl + 2\,IO_4^- + 4\,H^+ + 4\,Br^- = 3C_6H_5Cl + 3N_2 + 2IBr_2^- + 8H_2O \\
3\,C_6H_4(OH)_2 + IO_4^- + 2\,H^+ + 2\,Br^- = 3\,C_6H_4O_2 + IBr_2^- + 4\,H_2O.
\end{array}$$

EXPERIMENTAL

Potassium meta-periodate was prepared by the method of BAHL AND SINGH[1]. A known weight of each substance was taken in a conical flask and about 25 ml of water, 5 ml of concentrated hydrochloric acid, 20 g of potassium bromide and 5 ml of carbon tetrachloride added to it. The mixture was diluted to about 100 ml with water and titrated against standard potassium meta-periodate solution. The conical flask was stoppered and vigorously shaken during the titration; the carbon tetrachloride layer acquired purple colour due to iodine. Addition of small volumes of the meta-periodate solution was continued, shaking vigorously after each addition, until the carbon tetrachloride layer was faintly violet. The meta-periodate was then added dropwise, with shaking after the addition of each drop, until the carbon tetrachloride layer became colourless. The end-point was very sharp.

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[1] BAHL AND SINGH, *J. Ind. Chem. Soc.* 17 (1940) 167.

Mercurous chloride, sodium sulphite and ferrous sulphate were pre-oxidised with 10 ml of 0.5*M* iodine monochloride solution before titration.

From the volume of potassium meta-periodate used, corresponding to the end point in each titration, the amount of each substance was calculated. The results are given in the following tables:

TABLE I

Potassium iodide			Arsenious oxide		
KI taken g	*M*/60 KIO_4 ml	KI found g	As_2O_3 taken g	*M*/60 KIO_4 ml	As_2O_3 found g
0.0830	10.00	0.0830	0.0990	20.00	0.0990
0.1079	13.00	0.1079	0.1436	29.10	0.1440
0.1495	18.10	0.1502	0.2128	43.10	0.2133
0.1827	22.00	0.1826	0.2376	48.10	0.2380

Tartar emetic			Stannous chloride		
Tartar emetic taken g	*M*/60 KIO_4 used ml	Tartar emetic found g	$SnCl_2.2H_2O$ taken g	*M*/60 KIO_4 used ml	$SnCl_2.2H_2O$ found g
0.3338	20.70	0.3454	0.1944	17.20	0.1941
0.4173	25.80	0.4306	0.2780	24.60	0.2776
0.5511	34.00	0.5674	0.3051	27.00	0.3047
0.7682	47.40	0.7911	0.3300	29.20	0.3295

Mercurous chloride			Sodium sulphite		
Hg_2Cl_2 taken g	*M*/60 KIO_4 used ml	Hg_2Cl_2 found g	Na_2SO_3 taken g	*M*/60 KIO_4 used ml	Na_2SO_3 found g
0.3000	12.70	0.2998	0.1226	19.40	0.1222
0.5000	21.20	0.5005	0.1855	29.40	0.1853
0.6000	25.40	0.5997	0.2473	39.30	0.2476
0.6500	27.50	0.6492	0.3095	49.30	0.3106

TABLE I (continued)

Sodium thiosulphate			Sodium tetrathionate		
$Na_2S_2O_3.5H_2O$ taken g	$M/60$ KIO_4 used ml	$Na_2S_2O_3.5H_2O$ found g	$Na_2S_4O_6$ taken g	$M/60$ KIO_4 used ml	$Na_2S_4O_6$ found g
0.0527	17.00	0.0527	0.0351	18.20	0.0351
0.0837	27.00	0.0837	0.0457	23.70	0.0457
0.1023	33.00	0.1023	0.0596	30.90	0.0596
0.1147	37.10	0.1150	0.0768	39.80	0.0768

Ferrous sulphate			Potassium thiocyanate		
$FeSO_4.7H_2O$ taken g	$M/60$ KIO_4 used ml	$FeSO_4.7H_2O$ found g	KCNS taken g	$M/60$ KIO_4 used ml	KCNS found g
0.3620	13.00	0.3611	0.0323	20.10	0.0325
0.5562	20.10	0.5584	0.0437	27.10	0.0438
0.7520	27.00	0.7501	0.0534	33.00	0.0533
0.8361	30.10	0.8361	0.0809	50.20	0.0811

TABLE II

Hydrazine sulphate			Phenylhydrazine hydrochloride		
$N_2H_4.H_2SO_4$ taken g	$M/60$ KIO_4 used ml	$N_2H_4.H_2SO_4$ found g	$C_6H_5NH.NH_2.HCl$ taken g	$M/60$ KIO_4 used ml	$C_6H_5NH.NH_2.HCl$ found g
0.0650	20.00	0.0650	0.0470	13.00	0.0470
0.0845	26.00	0.0845	0.0723	20.00	0.0723
0.1105	34.00	0.1105	0.0976	26.80	0.0970
0.1495	46.00	0.1495	0.1554	43.10	0.1557

Hydroquinone		
$C_6H_4(OH)_2$ taken g	$M/60$ KIO_4 used ml	$C_6H_4(OH)_2$ found g
0.1100	19.90	0.1095
0.1485	27.00	0.1485
0.1760	32.00	0.1760
0.2365	43.00	0.2365

From the above results it is evident that potassium iodide, arsenious oxide, antimonous oxide, stannous chloride, mercurous chloride, sodium sulphite,sodium thiosulphate, sodium tetrathionate, ferrous sulphate, potassium thiocyanate, hydrazine sulphate, phenyl hydrazine hydrochloride and hydroquinone can be determined quantitatively by the iodine bromide method, using potassium meta-periodate as volumetric reagent.

SUMMARY

Potassium meta-periodate has been used as an oxidising agent in acid medium for the volumetric estimations of potassium iodide, arsenious oxide, antimonous oxide, stannous chloride, mercurous chloride, sodium sulphite, sodium thiosulphate, sodium tetrathionate, ferrous sulphate, potassium thiocyanate, hydrazine sulphate, phenylhydrazine hydrochloride and hydroquinone by the iodine bromide method. Carbon tetrachloride is used as an indicator. It is coloured pink during the titration and becomes colourless at the end-point due to the formation of stable iodine bromide complex IBr_2^-, which does not dissociate, in the presence of a large excess of bromide ion.

RÉSUMÉ

L'emploi du métaperiodate de potassium comme agent d'oxydation en milieu acide est proposé pour les dosages volumétriques de: iodure de potassium, anhydride arsénieux, anhydride antimonieux, chlorure d'étain(II), chlorure de mercure(I), sulfite de sodium, thiosulfate de sodium, tétrathionate de sodium, sulfate de fer(II), thiocyanate de potassium, sulfate d'hydrazine, chlorhydrate de phénylhydrazine et hydroquinone (méthode iode-bromure). Le tétrachlorure de carbone est utilisé comme indicateur; il est coloré en rose pendant la titration et devient incolore au point final. La décoloration est due à la formation du complexe stable IBr_2^-, non dissocié, en présence d'un gros excès d'ions bromhydriques.

ZUSAMMENFASSUNG

Kaliummetaperjodat wurde als Oxydationsmittel in saurem Medium bei der massanalytischen Bestimmung von Kaliumjodid, Arsentrioxyd, Antimontrioxyd, Zinndichlorid, Mercurochlorid, Natriumsulfit, Natriumthiosulfat, Natriumtetrathionat, Ferrosulfat, Kaliumthiocyanat, Hydrazinsulfat, Phenylhydrazin-hydrochlorid und Hydrochinon mit der Jodbromidmethode benutzt. Kohlenstofftetrachlorid wird als Indikator verwendet. Es ist während der Titration rosa gefärbt und wird am Endpunkt farblos, was der Bildung des stabilen Jodbromidkomplexes JBr_2^- zu zuschreiben ist, der in Gegenwart eines grossen Überschusses von Bromionen nicht dissoziiert.

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MACRO- AND MICRO-VOLUMETRIC DETERMINATION OF ANTHRANILIC ACID AND ITS APPLICATION IN INORGANIC QUANTITATIVE MACRO- AND MICRO-ANALYSIS

by

CH. CIMERMAN AND M. SELZER

Laboratory of Analytical Chemistry and Microchemistry, Hebrew Institute of Technology, Haifa (Israel)

INTRODUCTION

Anthranilic acid was introduced as an analytical reagent in the year 1933 by FUNK AND DITT who described gravimetric methods for the determination of zinc, cadmium[1], cobalt, nickel and copper[2] by means of sodium anthranilate. In a later work[3] they described also a volumetric procedure in which the anthranilic acid was dibrominated using a bromate-bromide solution and indigo carmine-styphnic acid as indicator.

DAY AND TAGGART[4] determined anthranilic acid by tribromination using an excess of bromate-bromide solution which was then back-titrated with thiosulfate solution to the starch-iodine end-point.

In a critical study of the above-mentioned methods, SHENNAN, SMITH AND WARD[5] obtained high results when working according to the conditions specified in the direct (dibromination) method of FUNK AND DITT. They therefore prefered the indirect (tribromination) method of DAY AND TAGGART, and tested the method on zinc anthranilate precipitates.

In 1942, FUNK[6] revised his gravimetric methods for the determination of zinc and cadmium by means of anthranilic acid, stating that these cations must be precipitated from boiling solutions, and not at room-temperature as proposed originally. Precipitation in the cold led to high results, due probably to occlusion of excess reagent by the precipitate.

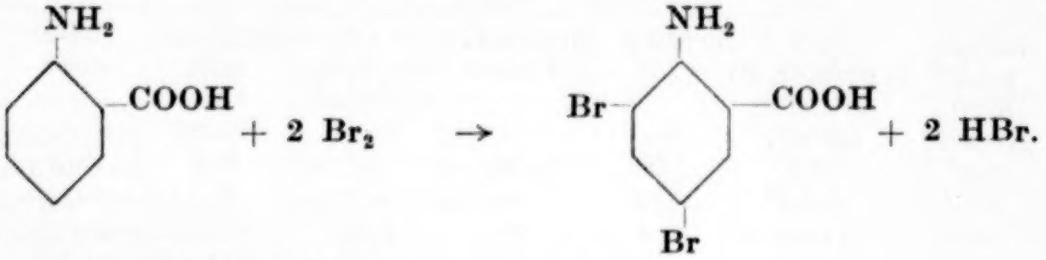
The aim of this research was:

1. To perform a critical study of the conditions of the macro-volumetric method for the determination of anthranilic acid by di- and tri-bromination, opinions in literature being discordant.
2. To elaborate an exact microvolumetric method based on this critical study.
3. To apply this method in quantitative inorganic micro-analysis to the determination of various elements (*e.g.* Co, Zn, Cd).

EXPERIMENTAL

Determination of anthranilic acid by dibromination (macro and micro)

The dibromination of anthranilic acid is based on the following reaction[7]:



Reagents and standard solutions

The reagents employed were:

1. Anthranilic acid solution I. (10 g anthranilic acid in 1 litre $4N$ HCl).
2. Anthranilic acid solution II. (0.2 g anthranilic acid in 1 litre $2.4N$ HCl).
3. Standard $0.1N$ potassium bromate-potassium bromide solution, (prepared by dissolving 2.7835 g $KBrO_3$ and 10 g KBr in water, and making up to 1 litre. This solution proved to be exactly $0.1N$ as checked by standardization against As_2O_3).
4. Standard $0.1N$ sodium thiosulfate solution. (This solution was standardized against $K_2Cr_2O_7$ and checked against the above bromate-bromide solution).
5. Indicator solutions:
   a. Methyl red (0.1% in 60% ethanol).
   b. Styphnic acid-indigo carmine (0.2 g styphnic acid and 0.2 g indigo carmine in 100 ml water).
   c. Fluoresceine (0.2% in ethanol).
   d. α-naphthoflavone (0.2% in ethanol).
   e. *p*-Ethoxychrysoidine (0.1% in ethanol).
   f. Quinoline yellow (0.5% in water).
   g. Starch solution 1%.
6. Potassium iodide solution 10%.

Bi-distilled water was used for all micro-titrations (including preparation of standard solutions employed in same).

Procedure followed for the macro-determination

For each titration 10 ml anthranilic acid solution I (containing 0.1 g anthranilic acid) were introduced into an Erlenmeyer flask of 250 ml capacity and diluted to 100 ml with water and hydrochloric acid to produce the required acidity, and then treated with a known volume of standard $0.1N$ potassium bromate-bromide solution. The reaction was allowed to proceed for the times stated, then 5 ml of a 10% potassium iodide solution were added and the liberated iodine was titrated with standard 0.1N thiosulfate solution in presence of starch as indicator.

1 ml 0.1N $KBrO_3$ solution → 3.4283 mg anthranilic acid.

TABLE I

DETERMINATION OF ANTHRANILIC ACID

Exp. No.	Anthranilic acid present mg	0.1N $KBrO_3$-KBr solution added ml	Acidity N	Reaction time min.	0.1N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	100	32.00	1.0	0	3.10	99.1	−0.9	−0.9
2.	100	32.00	2.2	0	2.35	101.7	+1.7	+1.7
3.	100	33.00	2.2	0	2.40	104.9	+4.9	+4.9
4.	100	30.00	2.2	10	0.30	101.8	+1.8	+1.8
5.	100	29.30	2.2	0	0.10	100.1	+0.1	+0.1
6.	100	29.25	2.2	0	0.15	99.8	−0.2	−0.2

Discussion

According to FUNK AND DITT a state of complete dibromination is not reached immediately with the acid concentration below 1.6N (Experiment No. 1).

As shown by experiments No. 2 — No. 4, the use of a large excess of potassium bromate solution or the prolongation of the time of reaction between the dibromination product and free (excess) bromine leads to a marked tendency towards tribromination. This is in agreement with the observations of SHENNAN, SMITH AND WARD[5].

Exact results can be obtained if the acidity is above 1.6N in order to ensure immediate and complete reaction, and a large excess of brominating solution is avoided. (Experiments No. 5—No. 6).

Remark: The experiments tabulated above (Table I) were carried out without indicator. The quantity of the bromate-bromide solution added was determined by a preliminary calculation.

After these experiments, various indicators, such as methyl red, styphnic acid — indigo carmine[3], fluoresceine[8], α-naphthoflavone[9], p-ethoxychrysoidine[9, 11] and quinoline yellow[10] (the last three being reversible indicators) were tested for their usefulness in showing the completion of the dibromination stage, *i.e.* the equivalence point.

All these indicators proved unsatisfactory, as they were either partially or completely destroyed by the bromine before the equivalence point or reacted too slowly, resulting in over-bromination of the anthranilic acid.

The relative error for macro quantities (100 mg anthranilic acid) was 0.6-2.2% when using p-ethoxychrysoidine as indicator. For the other indicators the error was higher still.

Owing to a tendency to tribromination of anthranilic acid and owing to a lack of a suitable indicator to show the exact end-point of dibromination, this

TABLE II

SOME RESULTS OBTAINED BY TITRATION OF ANTHRANILIC ACID WITH STANDARD 0.1N $KBrO_3$-KBr SOLUTION, USING VARIOUS INDICATORS. (Acidity: 2.2N).

Exp. No.	Indicator	Anthranilic acid present mg	0.1N $KBrO_3$-KBr solution added ml	0.1N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	methyl red	100	32.10	2.20	102.5	+2.5	+2.5
2.	methyl red	100	32.20	2.25	102.7	+2.7	+2.7
3.	styphnic acid-indigo carmine	100	32.00	2.30	101.8	+1.8	+1.8
4.	styphnic acid-indigo carmine	100	32.20	2.40	102.2	+2.2	+2.2
5.	fluorescein	100	32.30	2.25	103.0	+3.0	+3.0
6.	fluorescein	100	32.40	2.25	103.4	+3.4	+3.4
7.	α-naphthoflavone	100	30.10	0.25	102.3	+2.3	+2.3
8.	α-naphthoflavone	100	30.00	0.20	102.2	+2.2	+2.2
9.	*p*-ethoxychrysoidine	100	29.40	0.05	100.6	+0.6	+0.6
10.	*p*-ethoxychrysoidine	100	29.60	0.20	100.8	+0.8	+0.8
11.	*p*-ethoxychrysoidine	100	29.80	0.25	101.3	+1.3	+1.3
12.	*p*-ethoxychrysoidine	100	30.00	0.20	102.2	+2.2	+2.2
13.	quinoline yellow	100	32.40	2.30	103.2	+3.2	+3.2

method was not found sufficiently exact to be of practical use for the macro-volumetric determination of anthranilic acid.

In spite of negative results in the macro-titrations, some experiments were carried out on the micro-scale, using *p*-ethoxychrysoidine as the most suitable indicator.

Procedure followed for the micro-determination

For each titration 50 ml anthranilic acid solution II were introduced into an Erlenmeyer flask of 150 ml capacity. 1 g KBr and 2 drops of indicator were added. During the titration with standard 0.1N $KBrO_3$-KBr solution, the indicator being destroyed, new portions of 2 drops were added, making a total of 10 drops for a complete titration. On reaching a definite colour change from orange-red to yellow, 5 ml KI solution 10% were added and the liberated iodine back-titrated with standard 0.1N $Na_2S_2O_3$ solution.

Remark: The volumes of $KBrO_3$-KBr solution and $Na_2S_2O_3$ solution were measured with a micro-burette of 5 ml capacity, graduated to 1/100 ml and delivering about 100 drops per ml.

References p. 43.

Some characteristic results are given in Table III.

TABLE III

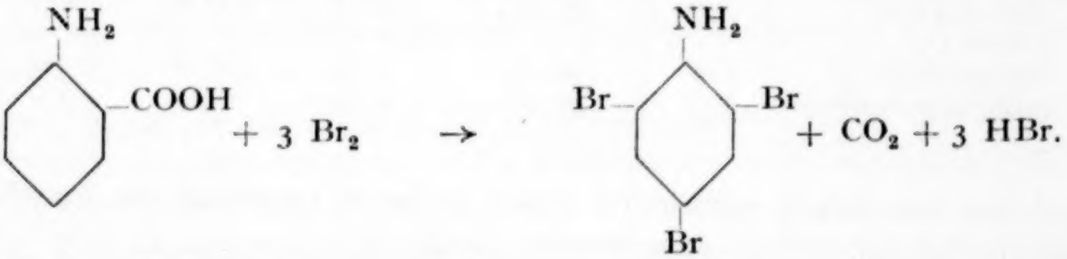
Exp. No.	Indicator	Anthranilic acid present mg	0.1N $KBrO_3$-KBr solution added ml	0.1N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	*p*-ethoxy-chrysoidine	10	3.01	0.030	10.22	+0.22	+2.2
2.	*p*-ethoxy-chrysoidine	10	3.05	0.030	10.35	+0.35	+3.5
3.	*p*-ethoxy-chrysoidine	10	3.10	0.035	10.51	+0.51	+5.1

Discussion

As Table III indicates, the results are too high (about 2-5%). The dibromination method is therefore not recommended for micro-quantities either.

Determination of anthranilic acid by tribromination (macro and micro)

The tribromination of anthranilic acid is based on the following reaction[7]:



The following factors were studied:
1. Quantity of anthranilic acid.
2. Excess of bromate-bromide solution.
3. Time of reaction.
4. Acidity.
5. Temperature of bromination.
6. Loss of bromine by volatilization.
7. Oxidation of anthranilic acid.

Reagents and standard solutions

The reagents employed were:

1. Anthranilic acid solutions in 4N HCl of various concentrations: 10 g/l, 5 g/l, 2 g/l and 1 g/l.
2. Standard 0.1N and 0.2N $KBrO_3$ - KBr solutions.
3. Standard 0.1N and 0.1N $Na_2S_2O_3$ solutions.

Apparatus for bromination

To eliminate bromine losses, a simple apparatus (Fig. 1 A) was used for the following experiments.

The apparatus consists of an Erlenmeyer flask (about 350 ml capacity for macro-titrations and about 125 ml for micro-titrations) connected to a separating funnel (about 50 ml capacity for macro-determinations and about 15 ml for micro-determinations) by a ground glass joint. The Erlenmeyer flask can be evacuated through the separating funnel (Fig. 1 B) by means of an ordinary laboratory filter-pump (aspirator). The apparatus must be able to keep a slight vacuum for at least 30 minutes.

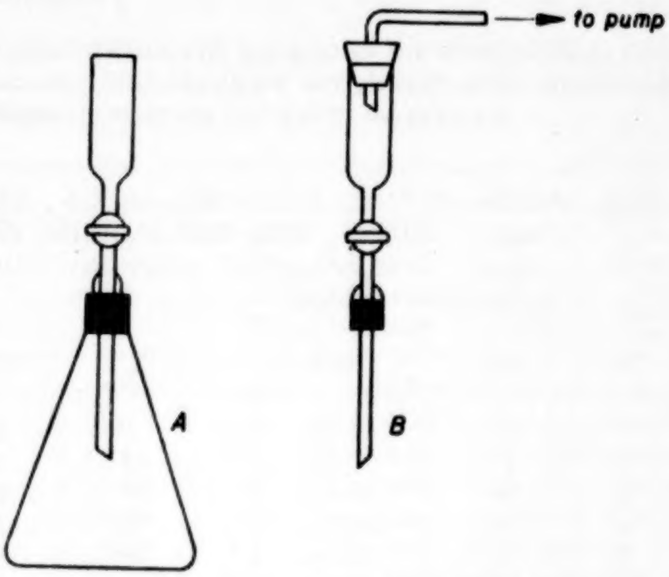


Fig. 1. Apparatus for bromination.

Procedure followed for the macro- and micro-determination

An aliquot portion of anthranilic acid solution was introduced into the Erlenmeyer flask of apparatus Fig. 1 A, which was then connected to the separating funnel and evacuated. The required excess of standard $KBrO_3$-KBr solution was introduced into the separating funnel and sucked into the flask by opening the stopcock slightly. The funnel was washed with a few milliliters of water.

After introducing the wash water, the flask was shaken and allowed to stand for 30 min at a temperature of 15-17° C. At the end of the bromination period, KI solution 10% (25 ml for macro- and 5 ml for micro- determination) was sucked into the Erlenmeyer flask without loss of bromine. After thorough shaking, the Erlenmeyer flask was opened, the solution diluted (to about 150 ml for macro-titrations and to about 70 ml for micro-titrations) and the iodine titrated with standard $Na_2S_2O_3$ solution.

1 ml $0.1N$ $KBrO_3$ solution → 2.2855 mg anthranilic acid.

Tables IV-X show caracteristic results obtained under various conditions.

Conclusion

1. As Table IV indicates, results are exact (maximum relative error ± 0.3%) when employing an excess of about 70-160% of $KBrO_3$-KBr solution.

2. Increase of acidity (above $2.2N$) or prolongation of reaction time (45 min instead of 30 min) has no influence on the results.

References p. 43.

TABLE IV

DETERMINATION OF 50 mg ANTHRANILIC ACID (10 ml OF SOLUTION CONTAINING 5 g/l), SHOWING INFLUENCE OF VARYING EXCESS OF $KBrO_3$-KBr SOLUTION, ACIDITY AND REACTION TIME. Reaction temperature: 15-17° C.

Exp. No.	Anthranilic acid present mg	0.1N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	Reaction time min.	Acidity N	0.1N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	50	23.95	9	30	2.2	2.42	49.21	−0.79	−1.6
2.	50	30.93	41	30	2.2	9.28	49.48	−0.52	−1.0
3.	50	32.93	50	30	2.2	11.26	49.53	−0.47	−0.9
4.	50	34.93	60	30	2.2	13.15	49.78	−0.22	−0.4
5.	50	36.92	69	30	2.2	15.10	49.87	−0.13	−0.3
6.	50	43.91	101	30	2.2	21.99	50.10	+0.10	+0.2
7.	50	49.90	128	30	2.2	27.99	50.08	+0.08	+0.2
8.	50	49.90	128	30	2.2	28.04	49.96	−0.04	−0.1
9.	50	56.88	160	30	2.2	34.95	50.12	+0.12	+0.2
10.	50	49.90	128	30	4.0	28.09	49.85	−0.15	−0.3
11.	50	49.90	128	45	2.2	27.95	50.17	+0.17	+0.3
12.	50	49.90	128	45	2.2	28.00	50.05	+0.05	+0.1

TABLE V

DETERMINATION OF 100 mg ANTHRANILIC ACID (10 ml OF SOLUTION CONTAINING 10 g/l), SHOWING INFLUENCE OF VARYING EXCESS OF $KBrO_3$-KBr SOLUTION. Reaction time: 30 min. Acidity: 2.2N.
Reaction temperature: 15-17° C.

Exp. No.	Anthranilic acid present mg	0.2N $KBrO_3$-KBr solution added ml	Excess $KBrO_3$-KBr solution %	0.2N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	100	36.87	69	15.00	99.97	−0.03	—
2.	100	41.47	90	19.52	100.33	+0.33	+0.3
3.	100	41.47	90	19.56	100.15	+0.15	+0.2
4.	100	50.15	129	28.22	100.24	+0.24	+0.2
5.	100	50.15	129	28.32	99.78	−0.22	−0.2

Conclusion

Results for the determination of 100 mg anthranilic acid are as exact as those for 50 mg (Table IV) at the same conditions.

References p. 43.

TABLE VI

DETERMINATION OF 5 mg ANTHRANILIC ACID (5 ml OF SOLUTION CONTAINING 1 g/l), SHOWING INFLUENCE OF VARYING EXCESS OF $KBrO_3$-KBr SOLUTION AND REACTION TEMPERATURE. Reaction time: 30 min. Acidity: 2.4*N*.

Exp. No.	Anthranilic acid present mg	0.1*N* $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1*N* $Na_2S_2O_3$ solution used ml	Reaction temperature °C	Anthranilic acid found mg	Difference mg	Relative error %
1.	5	3.70	69	1.518	15	4.987	−0.013	−0.3
2.	5	3.70	69	1.526	15	4.969	−0.031	−0.6
3.	5	3.70	69	1.534	15	4.950	−0.050	−1.0
4.	5	4.50	106	2.318	15	4.987	−0.013	−0.3
5.	5	4.50	106	2.315	15	4.994	−0.006	−0.1
6.	5	4.50	106	2.312	15	5.001	+0.001	—
7.	5	4.50	106	2.310	15	5.005	+0.005	+0.1
8.	5	5.00	128	2.818	15	4.987	−0.013	−0.3
9.	5	5.00	128	2.815	15	4.994	−0.006	−0.1
10.	5	5.00	128	2.810	15	5.005	+0.005	+0.1
11.	5	5.00	128	2.808	15	5.010	+0.010	+0.2
12.	5	6.00	174	3.818	15	4.987	−0.013	−0.3
13.	5	6.00	174	3.816	15	4.992	−0.008	−0.2
14.	5	6.00	174	3.810	15	5.005	+0.005	+0.1
15.	5	6.00	174	3.808	15	5.010	+0.010	+0.2
16.	5	7.00	220	4.812	15	5.001	+0.001	—
17.	5	7.00	220	4.805	15	5.017	+0.017	+0.3
18.	5	7.00	220	4.803	15	5.021	+0.021	+0.4
19.	5	7.00	220	4.801	15	5.026	+0.026	+0.5
20.	5	5.00	128	2.803	20	5.021	+0.021	+0.4
21.	5	5.00	128	2.797	20	5.035	+0.035	+0.7
22.	5	5.00	128	2.805	20	5.017	+0.017	+0.3
23.	5	5.00	128	2.773	28	5.090	+0.090	+1.8
24.	5	5.00	128	2.766	28	5.106	+0.106	+2.1
25.	5	5.00	128	2.768	28	5.101	+0.101	+2.0

Remarks: 1. In column "$Na_2S_2O_3$ solution used", the volume is given in 1/1000 ml, though the burette employed was only graduated to 1/100 ml. With the aid of a magnifying glass (meniscus reader), the burette-readings could easily be estimated within 0.002-0.003 ml. All readings were corrected according to the factor of the solution.

2. As exact results were obtained by careful titration with 0.1*N* standard solutions, more dilute solutions were not considered strictly necessary.

Conclusion

1. As table VI indicates, results are exact (maximum relative error ± 0.3%) when employing an excess of $KBrO_3$-KBr solution of about 105-175% for reaction temperature 15° C.

2. At temperatures of 20° C and above, results are too high.

References p. 43.

TABLE VII

DETERMINATION OF VARYING MICRO-QUANTITIES OF ANTHRANILIC ACID, USING AN OPTIMUM EXCESS OF $KBrO_3$-KBr SOLUTION. Reaction time: 30 min. Reaction temperature: 15-17° C. Acidity: 2.4N.

Exp. No.	Anthranilic acid present mg	0.1N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	10	9.30	112	4.937	9.972	−0.028	−0.3
2.	10	9.30	112	4.930	9.988	−0.012	−0.1
3.	10	9.30	112	4.932	9.983	−0.017	−0.2
4.	9	8.90	126	4.970	8.982	−0.018	−0.2
5.	9	8.90	126	4.950	9.028	+0.028	+0.3
6.	9	8.90	126	4.955	9.016	+0.016	+0.2
7.	8	8.50	143	5.005	7.988	−0.012	−0.2
8.	8	8.50	143	4.990	8.022	+0.022	+0.3
9.	8	8.50	143	4.992	8.018	+0.018	+0.2

Conclusion

Results for the determination of 8-10 mg anthranilic acid are as accurate as those for 5 mg (Table VI) at the same optimum conditions.

TABLE VIII

IN ORDER TO ASCERTAIN WHETHER MACRO-BROMINATION IS POSSIBLE IN AN ORDINARY GLASS-STOPPERED ERLENMEYER FLASK AS WELL, SOME EXPERIMENTS WERE CARRIED OUT, USING AN ERLENMEYER FLASK OF 250 ml CAPACITY. Reaction time: 30 min. Acidity: 2.2N. Temperature: 17° C.

Exp. No.	Anthranilic acid present mg	0.2N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.2N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Difference mg	Relative error %
1.	100	36.87	69	15.00	99.97	−0.03	—
2.	100	41.48	90	19.50	100.45	+0.45	+0.5
3.	100	43.85	100	21.80	100.79	+0.79	+0.8
4.	100	49.85	128	27.75	101.02	+1.02	+1.0

Conclusion

In an ordinary glass-stoppered Erlenmeyer flask, the results obtained are generally too high, probably owing to the volatilization of bromine which occurs on opening the flask for the addition of the bromate-bromide solution and the potassium iodide solution.

In order to determine the bromine losses due to volatilization as a function of time, the following experiments were carried out at a constant temperature of 20°C.

Into a small bottle of 100 ml capacity, having a narrow neck of about 15 mm diameter, were introduced 3.00 ml 0.1*N* $KBrO_3$-KBr solution and 7 ml 2.4*N* HCl. The bottle was left open for the times stated (Table IX); 5 ml KI 10% solution were added, and the liberated iodine was titrated with 0.1*N* thiosulfate solution.

TABLE IX

VOLATILIZATION OF BROMINE

Exp. No.	0.1*N* $KBrO_3$-KBr solution added ml	time of volatilization min.	0.1*N* $Na_2S_2O_3$ solution used ml	Volatilization of bromine %
1.	3.00	0	3.00	—
2.	3.00	½	2.99	0.3
3.	3.00	1	2.98	0.7
4.	3.00	3	2.97	1.0
5.	3.00	5	2.95	1.7

Conclusion

The loss of bromine due to volatilization increases with time, already causing a pronounced error in 30 sec.

GENERAL DISCUSSION OF TABLES IV—IX

1. As stated by DAY AND TAGGART[4], the rate and completeness of bromination depends on the excess of the brominating solution. This is clearly shown by Table IV. For a reaction time of 30 min, the minimum excess of bromate solution in macrotitration is about 70% (Table IV. Exp. No. 5). Increasing the reaction time or acidity has no adverse effect (Table IV. Exp. No. 10-No. 12).

2. Tables IV-VII show some titration results of various amounts of anthranilic acid and the influence of a varying excess of bromate solution and reaction temperature on the precision of the results.

In macrotitrations, for 50 mg anthranilic acid, it is convenient to use 0.1*N* standard solutions. For 100 mg anthranilic acid, the use of 0.2*N* standard solutions is recommended.

The optimum excess of $KBrO_3$-KBr solution in macrotitration is about 70-160%.

In microtitration, the minimum amount of anthranilic acid determinable is 5 mg. For lower quantities variable results were obtained. Exact results are also obtained for higher quantities, *e.g.* up to 10 mg (Table VII). Higher quantities than 5 mg merely cause inconvenience, when using a 5 ml burette, as it must be filled twice.

The optimum excess of $KBrO_3$-KBr solution in microtitration is about 105-175%.

3. The optimum reaction temperature is 15° C ± 2° C (Table VI). At temperatures of 20° C and above, the results were too high, probably owing to the oxidation of the anthranilic acid molecule by excess bromine. This is in accordance with the opinion of DAY AND TAGGART[4]. It is not recommended to work at a temperature lower than 10° C, as the reaction velocity is then too low[4].

4. Bromine losses due to volatilization were entirely eliminated by using the brominating apparatus shown in Fig. 1. Titrations carried out in an ordinary glass-stoppered Erlenmeyer flask (Table VIII) gave high results owing to the volatilization of bromine.

Based on the study of all factors influencing the precision of the results, the following elaborated method for microvolumetric determination of anthranilic acid is recommended:

Procedure

Introduce 5-10 ml 2.4-4*N* hydrochloric acid solution containing about 5 mg anthranilic acid into the Erlenmeyer flask of 125 ml capacity of the brominating apparatus (Fig. I). Connect the flask to the separating funnel and evacuate. Introduce into the funnel the optimum excess of 0.1*N* $KBrO_3$-KBr solution (105-175%), calculated according to a preliminary test as described below. Suck this brominating solution into the flask by opening the stopcock slightly. Wash the funnel with about 5 ml bidistilled water. After introducing the wash water, a slight vacuum must remain in the Erlenmeyer flask. Shake and let stand for 30 minutes at a temperature of 15° ± 2° C. At the end of the bromination period, suck into the Erlenmeyer flask 5 ml KI 10% solution by the procedure used above, thus avoiding loss of bromine.

After thorough shaking, open the Erlenmeyer flask, dilute to about 70 ml with bi-distilled water, and titrate the iodine liberated with standard 0.1 *N* thiosulfate solution measured from a microburette, graduated to 1/100 ml and delivering about 100 drops per ml, in presence of starch as indicator.

1 ml 0.1*N* $KBrO_3$-KBr solution → 2.2855 mg anthranilic acid.

The time necessary for one determination is about 1 hour.

References p. 43.

Preliminary test by the dibromination method for the calculation of the optimum excess of $KBrO_3$-KBr solution for the microtitration of anthranilic acid

Introduce into an Erlenmeyer flask of 150 ml capacity, 50 ml 2.4-4*N* hydrochloric acid solution containing 5-10 mg anthranilic acid, 1 g KBr and 2 drops of *p*-ethoxychrysoidine as indicator (0.1% in ethanol), and titrate with 0.1*N* standard $KBrO_3$-KBr solution, measured from a microburette graduated to 1/100 ml. As the indicator is destroyed, add new portions of 2 drops, making a total of 10 drops for a complete titration. On reaching a definite colour change from orange-red to yellow, add 5 ml KI 10% solution and back-titrate the liberated iodine with standard 0.1*N* $Na_2S_2O_3$ solution, measured from a microburette, in presence of starch as indicator.

As indicated by Table III, this procedure gives approximate results of + 2 → 5%. The optimum excess of $KBrO_3$-KBr solution in the exact tribromination micromethod, which is in the range of 105-175%, can be easily calculated from the results obtained by the preliminary test.

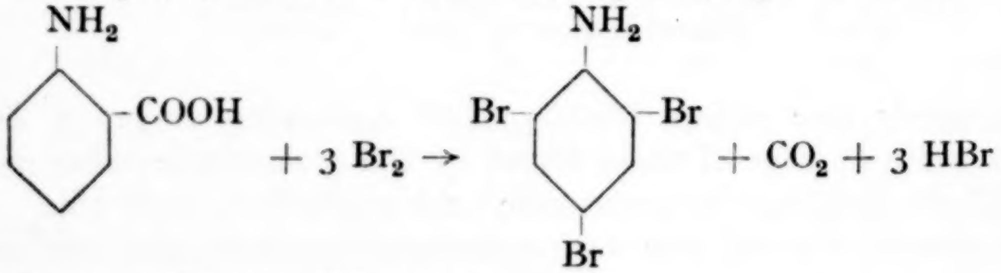
The time necessary for one preliminary test is about 30 min.

Application of anthranilic acid for the macro-volumetric determination of cobalt, zinc and cadmium

The volumetric method for the determination of anthranilic acid can be used in the inorganic quantitative analysis of various elements[3,5] (*e.g.* Co, Zn, Cd).

The cation is precipitated by anthranilic acid at suitable conditions. The precipitate is filtered, washed and dissolved in hydrochloric acid. The liberated anthranilic acid is determined by the volumetric tribromination method. The percentage of the cation is calculated according to the volume of standard $KBrO_3$-KBr solution which entered into the reaction. This is determined finally by iodometric titration.

Equations of reactions:

1. $Me^{+2} + 2\ C_6H_4(NH_2)COONa \rightarrow 2\ Na^+ + [C_6H_4(NH_2)COO]_2Me$
2. $[C_6H_4(NH_2)COO]_2Me + 2\ HCl \rightarrow MeCl_2 + 2\ C_6H_4(NH_2)COOH$
3. $KBrO_3 + 5\ KBr + 6\ HCl \rightarrow 3\ Br_2 + 3\ H_2O + 6\ KCl$
4. 

5. $Br_2 + 2\ KI \rightarrow 2\ KBr + I_2$
6. $I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$.

Me = Co, Zn, Cd, etc.

References p. 43.

Determination of cobalt

Solution employed: cobalt sulfate ($CoSO_4.7H_2O$) containing 1.073 g per litre. This titer is the average of those found by electrolysis (1.074 g/l) and by the gravimetric anthranilic acid method of FUNK AND DITT[2] (1.072 g/l).

In an aliquot portion of 50 ml, cobalt was precipitated by anthranilic acid according to the method of FUNK AND DITT[2]. The cobalt anthranilate precipitate was filtered through paper; after washing, the precipitate was dissolved in 3*N* HCl, and the filtrate collected in a 100 ml measuring flask. The filter paper was washed with 3*N* HCl, and the measuring flask made up to 100 ml, using the same acid.

The anthranilic acid was determined in an aliquot portion of 25 ml by the volumetric tribromination method in the manner described above. (Procedure followed for the macro and micro-determination).

1 ml 0.1*N* $KBrO_3$ solution → 0.4912 mg Co.

TABLE X

DETERMINATION OF COBALT

Exp. No.	Co present mg	0.1*N* $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1*N* $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Co found mg	Co difference mg	Relative error %
1.	13.41	50	83	22.75	62.28	13.39	−0.02	−0.2
2.	13.41	50	83	22.72	62.35	13.40	−0.01	−0.1
3.	13.41	50	83	22.65	62.51	13.43	+0.02	+0.2
Average					62.38	13.41	—	—

Conclusion

The results are exact (maximum relative error ± 0.2%).

Determination of zinc

Solution employed: zinc sulfate ($ZnSO_4.7H_2O$) containing 0.9422 g Zn per litre. The titer is the average of those found by the gravimetric oxine method (0.9420 g/l) and the gravimetric anthranilic acid method[6] (0.9424 g/l).

In an aliquot portion of 50 ml, zinc was precipitated by anthranilic acid according to the method of FUNK from a boiling solution[6]. The zinc anthranilate precipitate was treated exactly as the cobalt anthranilate precipitate in the determination of cobalt. 1 ml 0.1*N* $KBrO_3$ solution → 0.5448 mg Zn.

References p. 43.

TABLE XI

DETERMINATION OF ZINC

Exp. No.	Zn present mg	0.1 N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1 N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Zn found mg	Zn difference mg	Relative error %
1.	11.77	50	131	28.37	49.44	11.78	+0.01	+0.1
2.	11.77	50	131	28.32	49.55	11.81	+0.04	+0.3
3.	11.77	50	131	28.37	49.44	11.78	+0.01	+0.1
Average					49.48	11.79	+0.02	+0.2

Conclusion

The results are exact (maximum relative error + 0.3%).

Determination of cadmium

Solution employed: cadmium sulfate ($CdSO_4$ anhydrous) containing 1.3625 g Cd per litre. The titer is the average of those found by the gravimetric oxine method (1.3646 g/l)and the gravimetric anthranilic acid method[6] (1.3604 g/l).

Remark: According to DUVAL[12], the cadmium oxinate precipitate was dried at 280-380° C, since at 130° C, as indicated in the original method of BERG[13], it still energetically retains about 2 mg water and oxine[12].

In an aliquot portion of 50 ml, cadmium was precipitated by anthranilic acid according to the method of FUNK[6]. The cadmium anthranilate precipitate was treated exactly as the cobalt anthranilate precipitate in the determination of cobalt

1 ml 0.1N $KBrO_3$ solution → 0.9367 mg Cd

TABLE XII

DETERMINATION OF CADMIUM

Exp. No.	Cd present mg	0.1 N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1 N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Cd found mg	Cd difference mg	Relative error %
1.	17.03	40.0	120	21.83	41.53	17.02	−0.01	−0.1
2.	17.03	40.0	120	21.80	41.60	17.05	+0.02	+0.1
3.	17.03	40.0	120	21.77	41.66	17.08	+0.05	+0.3
Average					41.60	17.05	+0.02	+0.1

Conclusion

The results are exact (maximum relative error ± 0.3%).

Application of anthranilic acid for the micro-volumetric determination of cobalt, zinc and cadmium

Micro-determination of cobalt

Solution employed: cobalt sulfate ($CoSO_4.7H_2O$) containing 1.788 mg Co per gram solution. This titer was determined as follows:

About 2 ml of the cobalt sulfate solution were introduced into a Schwarz-Bergkampf filter-beaker and the exact amount (expressed in grams) found by weighing. Then the cobalt was determined according to the microgravimetric method of WENGER, CIMERMAN AND CORBAZ[14], using anthranilic acid.

For the volumetric determination an aliquot portion (about 0.7 ml) of the cobalt sulfate solution was introduced into a tared microbeaker of 10 ml capacity and weighed. The cobalt was precipitated with anthranilic acid and washed as in the above microgravimetric procedure, using the filter-stick technique of EMICH[15] for filtration and washing.*

(Care should be taken to suck the precipitate as dry as possible. Remaining traces of alcohol may cause high results owing to their oxidation by bromine).

The precipitate was dissolved and washed with small portions of hot 4*N* HCl, and the solution sucked into the brominating flask (Fig. 2). The total volume of hydrochloric acid for dissolving and washing was about 10 ml.

The determination was finished by the tribromination method as outlined in the procedure for anthranilic acid (micro-method).

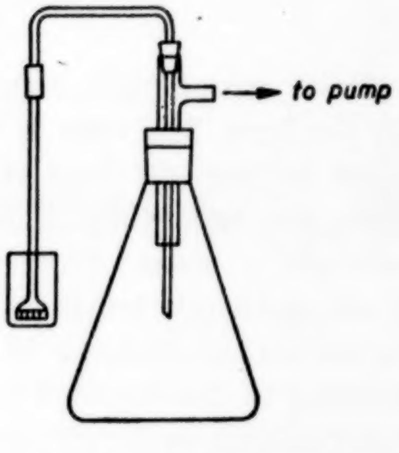


Fig. 2. Apparatus for filtration.

TABLE XIII

MICRO-DETERMINATION OF COBALT

Exp. No.	Co present mg	0.1 *N* $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1 *N* $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Co found mg	Co difference mg	Relative error %
1.	1.224	5.00	101	2.510	5.691	1.223	−0.001	−0.1
2.	1.305	6.00	126	3.350	6.056	1.302	−0.003	−0.2
3.	1.288	6.00	129	3.370	6.011	1.292	+0.004	+0.3

---

* The filter-stick used was made of glass, having the following dimensions: Diameter of filter 11 mm, outside diameter of stem 3.5 mm, inside diameter 2 mm, height of stem 110 mm.

Conclusion

The results are exact (maximum relative error ± 0.3%).

Micro-determination of zinc

Solution employed: zinc sulfate ($ZnSO_4.7\ H_2O$) containing 1.4375 mg Zn per gram solution. This titer is the average of those found by the microgravimetric methods of CIMERMAN AND WENGER a) with anthranilic acid[16,17] (1.437 mg/g) and b) with oxine[18] (1.438 mg/g).

For the volumetric determination an aliquot portion (about 0.8-0.9 ml) of the zinc sulfate solution was introduced into a tared microbeaker of 10 ml capacity and weighed. The zinc was precipitated by anthranilic acid from the boiling solution and washed as in the above microgravimetric procedure[16,17]. The zinc anthranilate precipitate was treated exactly as the cobalt anthranilate precipitate in the determination of cobalt.

TABLE XIV

MICRO-DETERMINATION OF ZINC

Exp. No.	Zn present mg	0.1 N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1 N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Zn found mg	Zn difference mg	Relative %
1.	1.349	5.00	102	2.516	5.677	1.353	+0.004	+0.3
2.	1.398	6.00	134	3.432	5.869	1.399	+0.001	+0.1
3.	1.258	5.00	117	2.697	5.264	1.255	−0.003	−0.2

Conclusion

The results are exact (maximum relative error ± 0.3%).

Micro-determination of cadmium

Solution employed: cadmium sulfate ($CdSO_4$ anhydrous) containing 1.987 mg Cd per gram solution. This titer is the average of those found by the microgravimetric method of WENGER, CIMERMAN AND WYSZEWIANSKA[19] with oxine (1.986 mg/g) and by the microgravimetric method of WENGER AND MASSET[20] with anthranilic acid (1.988 mg/g).

Remark: The cadmium oxinate precipitate was dried at 205° C for 45 min.

For the volumetric determination an aliquot portion (about 1.0-1.1 ml) of the cadmium sulfate solution was introduced into a tared microbeaker of 10 ml capacity and weighed. The cadmium was precipitated from the boiling solution by anthranilic acid and washed as in the above microgravimetric procedure[20]. The cadmium anthranilate precipitate was treated exactly as the cobalt anthranilate precipitate in the determination of cobalt.

TABLE XV

MICRO-DETERMINATION OF CADMIUM

Exp. No.	Cd present mg	0.1 N $KBrO_3$-KBr solution added ml	Excess of $KBrO_3$-KBr solution %	0.1 N $Na_2S_2O_3$ solution used ml	Anthranilic acid found mg	Cd found mg	Cd difference mg	Relative error %
1.	2.226	5.00	110	2.616	5.449	2.233	+0.007	+0.3
2.	2.216	5.00	111	2.629	5.419	2.221	+0.005	+0.2
3.	2.008	5.00	133	2.849	4.916	2.015	+0.007	+0.3

Conclusion

The results are exact (maximum relative error + 0.3%).

SUMMARY

The authors performed a critical study of the macro-volumetric method for the determination of anthranilic acid by di- and tri-bromination. Preference was given to the tribromination method, as it was found to be more precise.

On the basis of this critical study, the authors have elaborated an exact micro-volumetric method by tribromination.

This method was applied in inorganic quantitative microanalysis for the determination of cobalt, zinc and cadmium.

RÉSUMÉ

Les auteurs ont fait une étude critique de la macrométhode volumétrique pour la détermination de l'acide anthranilique par di- et tri-bromuration. Ils donnent la préférence à la méthode par tribromuration, celle-ci étant plus précise.

En se basant sur cette étude critique, les auteurs ont élaboré une microméthode volumétrique exacte par tribromuration.

Ils ont appliqué la méthode élaborée en microanalyse inorganique quantitative pour la détermination du cobalt, zinc et cadmium.

ZUSAMMENFASSUNG

Die Verfasser führten eine kritische Untersuchung der makrovolumetrischen Methode zur Bestimmung der Anthranilsäure durch Di- und Tribromierung aus.

Der Tribromierungsmethode wurde der Vorzug gegeben, da sie sich als genauer erwies.

Auf Grund dieser kritischen Untersuchung haben die Verfasser eine genaue mikrovolumetrische Tribromierungsmethode ausgearbeitet.

Die Methode wurde in der anorganischen quantitativen Mikroanalyse zur Bestimmung von Kobalt, Zink und Kadmium angewandt.

References p. 43.

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ADSORPTION INDICATORS — V

by

G. MANNELLI AND M. L. ROSSI

Istituto di Chimica Analitica della Università, Firenze (Italia)

Many authors have turned their attention to adsorption indicators liable to be used in an acid medium. KOLTHOFF[1] first of all used acetic acid in amounts varying from 1 to 5 ml with 4*N* concentration and he obtained good results. After him many authors have studied the behaviour of some indicators in the presence of several acids, such as nitric, phosphoric, oxalic and acetic acid[2]. Diphenylamine has been used as indicator in the presence of concentrated sulphuric acid[3]. With several indicators previously studied we have also worked in a weak nitric acid medium with satisfactory results[4].

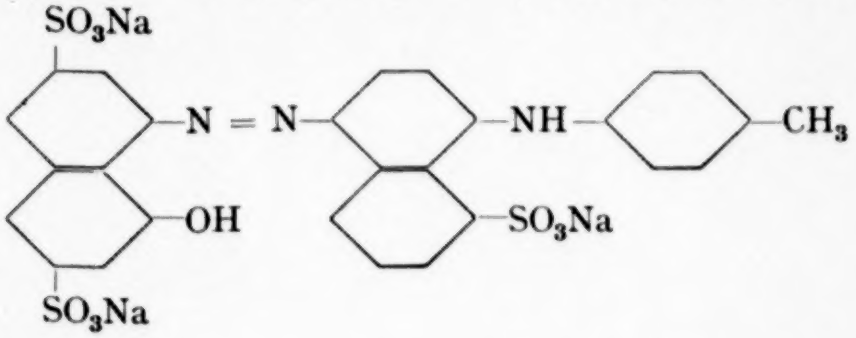
On the contrary the known indicators acting in an ammoniacal medium are less numerous. FAJANS AND WOLFF[5] have shown that in a very slight ammoniacal solution fluorescein gives good results.

MEHROTRA[6] has proposed the resorcinol-quinoline and the bromphenol blue, but always in a slight ammoniacal solution.

According to KOLTHOFF, who has studied the behaviour of eosin in the presence of NH_3, it seems that the inability of adsorption indicators to act in an ammoniacal medium must be investigated in the fact that the "oxidril ions" displace the colouring ion from the surface of silver iodide.

With the aim of increasing the knowledge about the adsorption indicators we have turned our attention to a new colouring substance, the behaviour of which we wish to make known even if its use is confined to argentometric determination of I_2.

This substance, known as "Blue sulphone acid B" is the sodium salt of the 1-hydroxy-naphthyl-8-azo-5′-(*p*-toluylamino)-naphthyl-3-6-4′-trisulphonic acid:



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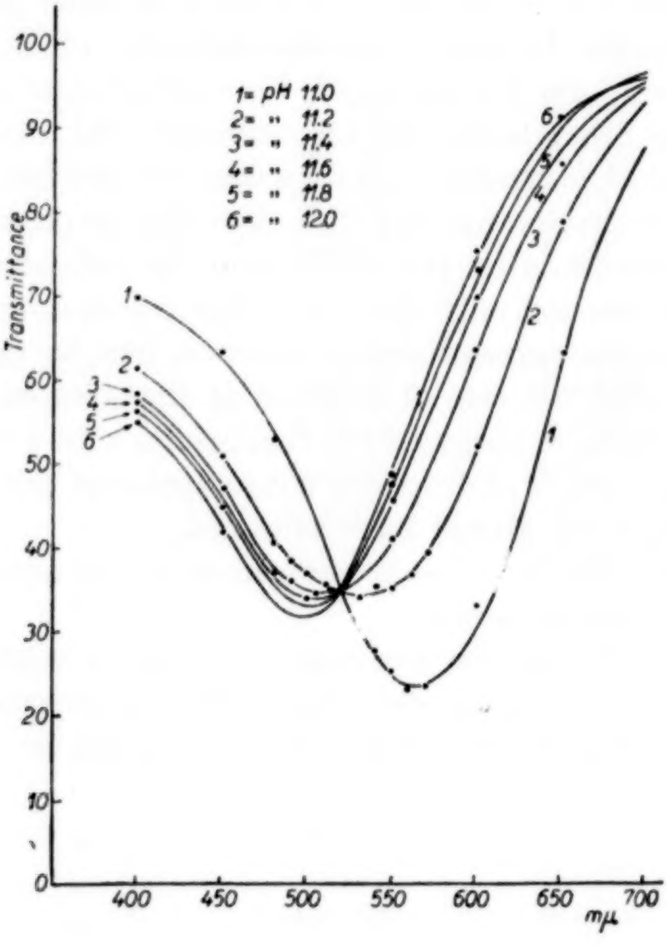
This substance, really, acts very well either in an acid medium or in a strongly alkaline medium.

The solution of the indicator is of an intense violet colour which assumes a blue-green colour when, by degrees, the silver halide is formed inside the liquid itself. This blue-green colour turns sharply to an apple-green colour at the equivalent point.



Following KOLTHOFF's hypothesis, we have executed, analogously to MEHROTRA, a test to demonstrate the perfect stability of the colouring absorbed by the silver salt. After having precipitated the silver iodide, this has been washed three times for decantation with distilled water, and N HNO_3 or N NH_4OH has been added. Even with energetic shaking the liquid remained colourless and we only noticed a slight variation of the colour of the precipitate, which in acid medium is sharply green, while in the presence of ammonia it assumes a green colour showing a slight tendency to blue.

Although we cannot consider Blue sulphone acid B as a neutralization indicator, nevertheless it presents some change of colour according to the pH of the solution.

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It assumes a perfect blue colour till pH 3, between pH 3 and pH 4 it becomes violet-blue, while it is of an intense violet between pH 4 and pH 10. For pH greater than 11 the colouring firstly becomes lilac and then red.

Although the solution assumes a different colour according to the variation of pH, the colour which we obtain at the equivalent point is nearly the same apple-green colour. Working in an alkaline medium a blue-violet colouring is initially observed, which we also observe in a neutral medium.

When the alkalinity of the solution containing I^- ions is not produced by ammonium hydroxide it is necessary to remove it in order to avoid the precipitation of the silver oxide. In such a case the indicator which we propose is very good because it permits, on the one hand, the regulation of the pH value of the solution and, on the other hand, the argentometric titration.

The salty charge which forms in the solution does not interfere with the good development of the next determination and the colour change occurs at the end point. Under such circumstances, after the addition of the indicator, it is sufficient to add nitric acid to the solution until the red or lilac colour changes to a sharp blue and afterwards the usual argentometric titration can be carried out.

We have noticed that the rate of addition of the solution of silver nitrate is very important and we have obtained the best results with a rate of 45-50 drops a minute. For a larger number of drops the consumption of the titrating solution is lower than that which we should have obtained.

It is important that the titration be performed in one action, that is, without stopping it from beginning to end.

Blue sulphone acid B may be eventually used as a neutralization indicator between pH 11 and 12. We have determined the spectrophotometric curves in this range; they show a characteristic isosbestic point at 520 mμ (see Fig.).

Reagents employed

Blue sulphone acid B twice recrystallized and its 0.1% solution in water.
Silver nitrate from silver 1000$^0/_{00}$
Potassium iodide of Pfizer Co. twice recrystallized.

The solutions prepared at the desired concentrations have been standardized according to the usual methods. Purified sodium chloride has been used as primary standard.

HNO_3 N/10 added ml		KI g present	 found	 difference
1	N/100	0.1593	0.1586	$7 \cdot 10^{-4}$
2	,,	0.1593	0.1586	$7 \cdot 10^{-4}$
10	,,	0.1593	0.1586	$7 \cdot 10^{-4}$
15	,,	0.1593	0.1578	$1.5 \cdot 10^{-3}$
20	,,	0.1593	0.1588	$5 \cdot 10^{-4}$
HNO_3 N				
1	N/100	0.1593	0.1587	$6 \cdot 10^{-4}$
5	,,	0.1593	0.1586	$7 \cdot 10^{-4}$
10	,,	0.1593	0.1580	$1.3 \cdot 10^{-3}$
15	,,	0.1593	0.1583	$1 \cdot 10^{-3}$
H_3PO_4 N/10				
10	N/100	0.1593	0.1591	$2 \cdot 10^{-4}$
20	,,	0.1593	0.1588	$5 \cdot 10^{-4}$
30	,,	0.1593	0.1586	$7 \cdot 10^{-4}$
50	,,	0.1593	0.1589	$4 \cdot 10^{-4}$
70	,,	0.1593	0.1588	$5 \cdot 10^{-4}$
90	,,	0.1593	0.1588	$5 \cdot 10^{-4}$
NH_4OH N				
1	N/100	0.1593	0.1592	$1 \cdot 10^{-4}$
5	,,	0.1593	0.1593	0.00
10	,,	0.1593	0.1592	$1 \cdot 10^{-4}$
15	,,	0.1593	0.1590	$3 \cdot 10^{-4}$
20	,,	0.1593	0.1592	$1 \cdot 10^{-4}$
25	,,	0.1593	0.1593	0.00
30	,,	0.1593	0.1593	0.00
35	,,	0.1593	0.1593	0.00
40	,,	0.1593	0.1590	$3 \cdot 10^{-4}$
NaOH N/10	(+HNO_3)			
1	N/100	0.1593	0.1592	$1 \cdot 10^{-4}$
2	,,	0.1593	0.1593	0.00
5	,,	0.1593	0.1590	$3 \cdot 10^{-4}$
10	,,	0.1593	0.1593	0.00
15	,,	0.1593	0.1592	$1 \cdot 10^{-4}$
20	,,	0.1593	0.1591	$2 \cdot 10^{-4}$

SUMMARY

Blue sulphone acid B has been proposed as an adsorption indicator for I^--ions fit to be employed in strongly alkaline media.

RÉSUMÉ

Le bleu sulfone acide B, nouvel indicateur d'adsorption, est proposé pour les titrations argentométriques des ions I^-. Cet indicateur est particulièrement intéressant en solutionsrès alcalines.

ZUSAMMENFASSUNG

Ein neuer Adsorptionindikator, Blau Sulphonsäure B, wurde für argentometrische Titrierungen beschrieben. Die grosse Nützlichkeit des Indikators liegt darin dass er auch für sehr alkalinische Lösungen benutzt werden kann.

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THE DETERMINATION OF PLATINUM, PALLADIUM AND GOLD IN SILVER ASSAY BEADS

by

R. R. BAREFOOT AND F. E. BEAMISH

Department of Chemistry, University of Toronto, Toronto, Ontario (Canada)

INTRODUCTION

This investigation was undertaken in order to find a new procedure for the rapid analysis of silver beads which contain the soluble platinum metals. Some of the procedures which have been recorded in the literature and in the textbooks on fire assay are needlessly complicated and time-consuming, while others lead to inaccurate analyses. Very few data are available on the efficiencies of the separations and on the accuracies of the determinations of the small quantities of metals. Some of the systems chosen for this study contained palladium, platinum, iridium, rhodium, and gold. Gold was included since it is very frequently associated with the platinum metals in ores and concentrates.

EXPERIMENTAL

Reagents and apparatus

Samples of "pure" platinum, palladium, iridium, rhodium powdered sponges and gold foil were examined spectrographically and found to be free of impurities. Small amounts of the metals were prepared for weighing by either drying at 110° C or igniting in air at 600° C, followed by a reduction in hydrogen. Accurately weighed quantities of the metals were used in the preparation of silver beads.

The finely powdered silver that was used to form the silver beads was slightly contaminated with gold. A blank eliminated this error.

The lead buttons were formed from finely granulated lead; lead foil was used in some of the work.

Zinc dust which passed through a 200 mesh sieve was used for the reduction of platinum salts in the determination of platinum. An analysis of the material by A.C.S. methods showed that it contained 0.1% lead and 0.006% iron.

A Sartorius projection-reading, air-damped microbalance was used for most of the weighings.

The spectrographic tests and analyses were carried out on a Hilger medium quartz instrument equipped with an arc source unit.

Standard solutions

1. *Palladium*

A palladium chloride solution, which contained approximately 0.07 mg of palladium per ml, was standardized gravimetrically with dimethylglyoxime. Any palladium in the filtrate was determined spectrographically. 10.01 ml of solution contained 0.71 mg of palladium.

2. *Gold*

A solution of gold chloride was standardized by the hydroquinone method[3]. The filtrates were evaporated and tested spectrographically. 10.01 ml of solution contained 0.98 mg of gold.

Preparation of silver assay beads

Accurately weighed quantities of the platinum metals and gold were mixed with a weighed amount of powdered silver and 30 grams of granulated lead in a steel mould. Coherent lead buttons were formed under pressure. The quantities of the metals were those which correspond to the assays of those ores in which platinum and palladium predominate. The weight of the silver used for each bead was 100 mg.

The lead buttons, on preheated bone ash cupels, were placed in a furnace at a temperature of 930° C and cupelled.

It is important to note that in microgravimetric work of this type, a blank should be carried throughout the entire analysis. The blank helps to account for (1) the ash content of filter papers when these are burned, (2) the presence of silica due to the corrosion of the laboratory glassware by the chemicals used in the analysis, and (3) the presence of small quantities of impurities in the chemicals themselves. In the work reported here, a blank derived from the cupellation of a lead button which contained a weighed amount of silver but no platinum metals or added gold was carried through the analysis with each set of silver beads. The value of the blank was subtracted at the places which are indicated in the procedures which follow.

PARTING THE SILVER BEADS

Both sulfuric and nitric acids have been recommended as parting acids for silver beads which contain platinum metals and gold. The choice of the parting acids depends upon a number of factors. If the amount of gold present exceeds that of palladium, then most if not all of the palladium can be dissolved together with silver in nitric acid parting media of various strengths[9]. Some platinum also enters the liquid phase but as a colloidal suspension and not in the form of a dissolved constituent. In general, the residue must be inquarted two or three times with silver, cupelled and parted before all the palladium and platinum can be removed from the gold residue. Gold, rhodium and iridium are insoluble. Gold may be extracted from the residue by means of aqua regia, which will also dissolve any palladium and platinum not dissolved in the nitric media. It must be noted, however, that rhodium and iridium tend to be lost mechanically during the cupellation process, even if the two metals are present in very small amounts. It has been the experience of the authors that some rhodium and iridium are lost from beads in which the ratio of silver to rhodium + iridium is as high as 1000:1. Hence, it is good practice to avoid extra cupellations when these metals are known to be present. In addition, the analysis of the combined nitric acid extracts which contain silver, platinum and palladium is difficult. Many procedures call for the removal of the silver by precipitation as silver chloride as the first step in the analysis. Since silver is the major metal in solution, often being present in the ratio 100:1 silver:platinum metals, the precipitated silver chloride is badly contaminated with palladium and with platinum. This makes one or two reprecipitations of the silver chloride necessary. SCHOELLER AND POWELL[8] have recorded an old procedure[11] in which the nitric acid parting solution is evaporated to dryness; the platinum and palladium nitrates are decomposed by heat in the presence of the more stable silver nitrate which is subsequently dissolved in water. This procedure was investigated but found to be time-consuming and to produce large errors.

A critical study of the work of other researchers led to the conclusion that a preliminary parting of the bead with sulfuric acid is desirable. The use of sulfuric acid in the analysis of the system which contained silver, platinum, palladium, gold, rhodium, and iridium made several new separations possible and greatly improved and simplified the existing methods of analysis.

SULFURIC ACID PARTING

A treatment of the silver bead with hot concentrated sulfuric acid has the advantage of dissolving most of the silver, some of the palladium but none of the other metals under consideration if the proper conditions are used[2]. Two procedures are recorded in the literature for the separation of palladium and silver and the determination of the latter. The first depends upon the precipitation of the silver content of the solution as silver chloride. Again, since the quantity of silver salts in solution greatly exceeds that of palladium salts, palladium will contaminate the silver chloride precipitate. In the second procedure, the palladium is precipitated as the oxide at pH 6, filtered off, redissolved and reprecipitated as the dimethylglyoxime complex[1].

A new and much simpler determination of palladium was developed. It was found that palladium could be precipitated directly in the presence of silver sulfate by the addition of an aqueous solution of sodium dimethylglyoxime. After the precipitate has been washed, any error due to contamination with silver is negligible. Thus a clean separation of palladium from silver in the parting medium is effected in one operation.

ANALYSIS OF THE RESIDUE

The insoluble portion from the sulfuric acid parting contains gold, platinum, rhodium, iridium, the remainder of the palladium, a small quantity of silver and some other insoluble materials. The question of whether the parting residue should be inquarted and treated for the further extraction of palladium is important. In experiments 8 and 9, Table I, the parting residues were inquarted twice and the palladium in the combined parting acids of each was determined. The figures showed that a large portion of the palladium content remained in the residue. In addition, the extra cupellations increased the possibility of mechanical losses of the metals and of dissolving of platinum in the parting media. For these reasons, it is recommended that the residue should not be inquarted. A treatment of the residue with strong aqua regia will dissolve gold, platinum, palladium and silver; rhodium and iridium are insoluble. In the analysis of the aqua regia portions, the small quantity of silver present may be readily removed as silver chloride. It was decided that dimethylglyoxime should be retained as the reagent for palladium. HOLZER has shown[7] that, under the proper conditions, palladium may be separated from platinum by a single precipitation with aqueous dimethylglyoxime. WUNDER AND THURINGER[12] precipitated gold and palladium together by boiling a solution of the two metals with dimethylglyoxime. They reported that palladium and gold could not be separated from platinum in their procedure. A few tests by the present authors confirmed this statement. Previous researches carried on in this laboratory have shown that while gold is precipitated quantitatively as the metal by boiling a solution of gold chloride to which dimethylglyoxime has been added[10], the initial step in the reaction is the formation of an unstable precipitate of gold with the organic reagent. The precipitate was isolated but it decomposed readily on exposure to the air.

These facts led to the idea that palladium might be precipitated alone from a solution of the three metals by a mild treatment with aqueous dimethylglyoxime. A few experiments proved the idea to be sound. This is a new separation of palladium from gold and platinum. The palladium compound can be easily filtered off. The filtrate may be treated directly with hydroquinone for the separation of the gold from the platinum. If the gold is precipitated by hydroquinone before the palladium is removed, then the excess hydroquinone may interfere with the subsequent precipitation of palladium dimethylglyoxime[2].

The excess of hydroquinone and dimethylglyoxime in solution also interferes with the recovery of platinum as the metal, by reduction with sodium formate, or, as the sulfide by precipitation with hydrogen sulfide. However, it was found that the platinum could be precipitated directly from the solution by reduction with zinc without the prior removal of the organic compounds. This results not only in a saving of time but also in an improvement in accuracy. The details of the microgravimetric determination of platinum by zinc reduction have been reported in a recent publication[4].

The analysis for silver is often required in fire assay work. Silver can be determined gravimetrically in two different ways in the scheme which has been outlined. 1. The silver bead is weighed before parting with sulfuric acid. The weight of the other metals and insolubles is later subtracted from this value. 2. The filtrate from the determination of palladium is treated with hydrochloric acid and the silver chloride is collected and weighed. The correction for the small quantity of silver in the aqua regia portion is negligible.

PROCEDURE

The gravimetric determinations of the bead constituents are outlined below. The time required to complete an analysis can be reduced by arranging a series of weighings which results in the determination of one constituent (platinum in this procedure) by difference.

The silver bead to be analyzed was cleaned as much as possible of the adhering cupel material. It was placed in a 50 ml beaker, 2 ml of concentrated sulfuric acid were added, and the contents were heated carefully on a hot plate until the rapid evolution of bubbles had ceased and the solution began to turn orange. If the heating was prolonged, platinum was lost to the parting solution. The beaker was removed from the hot plate and set aside until the contents had cooled. The solution was diluted to 25 ml with cold water and filtered through a Whatman No. 42, 7 cm filter paper. The residue was transferred to the filter and washed with 50 ml of hot water. This wash was combined with the main filtrate in a 150 ml beaker. The beaker containing the filtrate was removed and set aside for the determination of palladium (A). The parting residue was washed five times with a hot 20% ammonium acetate solution and then three times with hot water. These washings were discarded.

Determination of palladium

The filtrate (A) was treated for the recovery of palladium. After dilution to a volume of about 100 ml with distilled water (chloride free), 3 ml of a 1% solution of sodium dimethylglyoxime in water were added. The contents were cooled in cold water (10° C) for one-half hour. The precipitate of palladium dimethylglyoxime was transferred without delay to a Whatman No. 42, 7 cm filter paper, then washed with 75 ml of hot water. The filter was dried, transferred to a tared porcelain micro-crucible and treated with six drops of "mixed acids" (a solution prepared by mixing 3 volumes of concentrated sulfuric acid, 3 volumes of nitric acid and 2 volumes of water. A previous research carried on in this laboratory showed that palladium dimethylglyoxime treated in this manner could be ignited in air without any loss of palladium). The crucible was heated slowly in a muffle furnace to char the contents. The temperature was then raised to 800° C and maintained for one-half hour. The crucible was cooled, heated in hydrogen, then in nitrogen and weighed. The blank was subtracted.

The results of a number of analyses of silver-palladium beads are shown in Table I, Nos. 1 to 3. A spectrographic examination of the recovered palladium revealed the presence of microgram quantities of silver, but the blank accounted for this. (The silver precipitate was due to the presence of a small quantity of chloride ion in the distilled water.) The silver was removed from the filtrate, and spectrographic tests were carried out to find any palladium which might have passed through the filter. Some of the filtrates contained palladium but the amount of metal did not exceed 10 μg in any instance.

Treatment of the residue

The filter which contained the parting residue was dried and placed in a tared porcelain micro-crucible. The crucible and contents were heated slowly in a muffle furnace to a temperature of 500° C. This temperature was maintained for a period of 1½ hours. The crucible was cooled, heated in hydrogen for 5 minutes, in nitrogen for 5 minutes and then cooled and weighed. The weight obtained after the blank was subtracted was made up of platinum, gold, rhodium, iridium, undissolved palladium, silver, and a small quantity of other insolubles.

The contents of the crucible were carefully transferred to a 50 ml beaker. A volume of 5 ml of aqua regia was added; the beaker was covered, placed on the steam bath and heated for 1 hour. 5 drops of aqua regia were added to the crucible which was placed in a covered beaker and heated on the steam bath for one-half hour. After the digestion period, the content of the crucible was washed into the beaker and the whole was then diluted with water to a volume of 15 ml. The mixture was filtered through a Whatman No. 42, 7 cm filter paper, and the filtrate was caught in a 50 ml beaker. The solids were transferred to the filter and washed with 10-15 ml of hot water. The washings were combined with the filtrate. The filter (B) was reserved.

100 mg of sodium chloride were added to the filtrate. The solution was then evaporated on a steam bath to a moist residue. Great care must be taken that the salts are not dried or baked during this evaporation and the subsequent operations. This precaution is necessary in order to avoid the decomposition of gold chloride. The moist salts were treated 4 times with 3 or 4 drops of concentrated hydrochloric acid, with careful evaporations between the additions. The

salts were then dissolved in 10 ml of 0.1 N hydrochloric acid; 10 ml of water were added, and the sample was heated on the steam bath to coagulate the small quantity of silver chloride which was precipitated. The mixture was filtered through the reserved filter (B). The precipitate was transferred to the filter and was washed with hot water until the volume of the combined filtrate and washings was about 50 ml. The filter (B) was placed in the original crucible and heated slowly to 600° C. The crucible was cooled, heated in hydrogen, cooled in nitrogen and weighed as before. The weight of the blank was subtracted. The resulting weight now represented the quantity of silver and aqua regia insolubles including rhodium and iridium in the original parting residue. When this weight was subtracted from the total weight of the sulfuric acid parting residue, then the combined weight of palladium, gold and platinum not dissolved in the sulfuric acid was obtained. Further, when the weight of palladium (A) in the parting acid was added, the combined weight of platinum, gold and palladium was found to be in good agreement with the combined weight of the starting materials.

The separation of palladium from gold and platinum

A volume of 10 ml of 0.1 N hydrochloric acid and one drop of nitric acid were added to the filtrate from the silver separation above. A volume of 2 ml of a 1% solution of aqueous sodium dimethylglyoxime was added slowly with stirring. The contents were chilled for one-half hour in cold water (10° C), removed and filtered immediately through a Whatman No. 42, 7 cm filter paper. The filtrate was caught in a 250 ml beaker. The precipitate of palladium dimethylglyoxime was transferred to the filter and washed with 80-90 ml of hot water; the washings were added to the filtrates. The palladium on the filters was determined gravimetrically as described previously.

A spectrographic examination of the recovered palladium showed an insignificant contamination due to gold, and that platinum was absent.

The separation of gold and platinum

The filtrate from the palladium determination was immediately acidified with concentrated hydrochloric acid. A volume of 1 ml of acid was added for each 100 ml of liquid. The resulting solution was then 0.1 N in hydrochloric acid. The sample was heated to boiling, 3 ml of a freshly prepared 1% solution of hydroquinone in water were added dropwise with stirring to the sample. The boiling was continued for 15 minutes. The sample was placed on a steam bath for one-half hour to coagulate the gold precipitate, and then was cooled and filtered immediately through a double filter composed of a Whatman No. 44, 5.5 cm filter paper superimposed on a No. 42, 7 cm paper. The gold was transferred to the filter with the aid of small sections of filter papers. The filter was washed with 40 ml of hot water. The filtrate and washings were set aside for determination of platinum. The filter was dried, placed in a tared micro-crucible and ignited in a muffle furnace. The crucible was cooled and weighed. As usual, an analysis blank was subtracted.

A spectrographic examination of the recovered gold showed only a negligible contamination of platinum.

The determination of platinum

The filtrate from the gold precipitation was evaporated to a volume of about 80 ml. The pH of the solution was adjusted to 1.3 by means of 1*N* sodium hydroxide solution. The platinum was then determined gravimetrically by reducing the platinum salts to the metal with powdered zinc. This procedure has been described in detail in a previous publication[4].

The analysis of some silver beads is shown in Table I, Nos. 4 to 11. As stated above it is possible to obtain the weight of platinum by difference as shown in Table I. If there is any doubt as to the accuracy of the results for gold and palladium, the determination of platinum should be carried out.

Table I, Nos. 12 to 15 also records the results of the analysis of a solution of palladium, gold and platinum which was prepared by mixing known volumes of the standard solutions mentioned earlier.

The determination of rhodium and iridium

Rhodium and iridium were included in the analysis of the system to learn their effect on the analysis for gold, platinum and palladium. The total weight of these metals was about 0.1 mg of which about 0.08 mg was rhodium. These two metals were insoluble in aqua regia as mentioned earlier. The determination of the combined weight of these two metals by a dry weighing of the residue from the aqua regia treatment was subject to relatively large errors and proved to be unsatisfactory. It was found that rhodium and iridium could be changed quantitatively to soluble double chlorides by chlorination at 600° C in the presence of sodium chloride. However, all of the existing methods for the separation of rhodium and iridium and the subsequent determination of iridium in microgram quantities were unacceptable. The titanium (III) chloride separation[5, 6] proved satisfactory for the separation of rhodium but no accurate method is available for the determination of small amounts of iridium in the presence of large proportions of titanium. The authors found that iridium could be isolated from the large quantity of titanium salts by treating the solution with 2-mercaptobenzothiazole and extracting the iridium-organic complex into chloroform. Further work on this procedure is being carried out in this laboratory.

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TABLE I

ANALYSIS OF SILVER BEADS FOR PALLADIUM, GOLD AND PLATINUM

For Nos. 1-11, Weight of silver taken = 100 mg

Expt.	Metals taken			METALS FOUND					
				Palladium mg			Gold	Platinum mg	
No.	Palladium mg	Gold mg	Platinum mg	Parting acid	Residue	Total	mg	By analysis	By difference
1	2.98	—	—	2.98		2.98			
2	2.71	—	—	2.70		27.0			
3	2.33	—	—	2.27		2.27			
4	—	2.13	3.86		Total Weight of Au + Pt —			6.58	Error = +0.59
5	—	0.85	1.23		,, ,, ,, ,, ,, —			2.28	Error = +0.20
*6	—	2.89	4.25				2.84		4.21
*7	—	1.41	1.24				1.41		1.17
*8	1.30	1.65	2.97	0.79		Total Wt. Pt, Au, Pd in residue —		5.05	Error = −0.08
*9	1.07	1.48	3.01	0.65		Total Wt. Pt, Au, Pd in residue —		4.89	Error = −0.02
*10	1.42	0.75	2.37	0.28	1.14	1.42	0.74	2.42	2.43
*11	0.74	1.07	1.64	0.22	0.54	0.76	1.10	1.64	1.62
12	0.71	0.98	1.99			0.75	1.01	2.04	
13	0.71	0.98	1.99			0.74	0.97	2.09	
14	0.71	0.98	1.99			0.72	1.00		
15	0.71	0.98	1.99			0.75	0.99		

* 0.1 mg Rh + Ir present in the silver bead.

ACKNOWLEDGEMENT

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SUMMARY

Certain errors associated with standard treatments of platinum metals — silver assay beads are described. Procedures are given for the isolation of pure palladium from the parting acid and from the residue. Methods for the determination of platinum by precipitation and by difference are incorporated in a procedure for the determination of gold, palladium and platinum.

RÉSUMÉ

Certaines erreurs, en relation avec les essais par voie sèche (métaux du groupe platine-argent) sont décrites, au sujet de la séparation du palladium.

Des méthodes de dosage du platine par précipitation et par différence sont incorporées au procédé de dosage or-palladium-platine.

ZUSAMMENFASSUNG

Gewisse Fehler, die mit der normalen Platinmetall-Silberkorn-Behandlung verbunden sind werden für die Isolierung von reinem Palladium aus dem Scheidewasser und aus dem Rückstand beschrieben. Methoden zur Bestimmung von Platin durch Ausfällungs- und Differenzmethoden werden in ein Verfahren zur Bestimmung von Gold, Palladium und Platin eingebaut.

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A RAPID COMBUSTION TECHNIQUE FOR THE DETERMINATION OF SMALL AMOUNTS OF SULPHUR AND HALOGENS IN ORGANIC LIQUIDS

by

P. GOUVERNEUR AND H. VAN DIJK

Koninklijke/Shell-Laboratorium, Amsterdam (Netherlands)

The determination of small amounts of sulphur and halogens in organic liquids is an old problem and several techniques have, to this end, been developed, most of which depend upon the combustion of a large amount of material. Techniques employing wick lamps are probably the most widely accepted but their application is limited to low boiling liquids. Combustion tube methods and wick-free quartz lamp methods offer better possibilities in this respect but present the problem of proper administration of sample without risk of explosions or incomplete combustion. Useful contributions in this field include

a) the addition of sample to a horizontal combustion tube in a fine stream[9] or in the form of a fine spray[3],

b) drop by drop addition to a vertical combustion tube[2,8], and

c) combustion through a wick-free quartz (VOIGT) lamp whether[1] or not[7] in combination with a short combustion section.

It is not the object of this contribution to discuss the merits and limitations of the above techniques, but rather to point to a simple solution which we have employed for a number of years in our laboratory in connection with the Shell-Braun quartz tube combustion unit recently described[5]. This technique was developed on the basis of preliminary experiments by PETERS AND CAMPANILE[6] and consists in the dropwise introduction of sample from a weighing pipette to a portion of the quartz tube which serves as a vaporization section. By proper heating of this section vaporization can be made to take place instantaneously so that each drop of sample received is vaporized before the next one enters. A rapid stream of air together with a high temperature section ensures complete combustion. The combustion gases are passed through a single ASTM lamp sulphur absorber. The technique, as described below, has been applied with uniform success to a variety of petroleum products ranging from gasolines to lubricating oils as well as to pure aromatics ranging from benzene to cumenes. The method is rapid as 5 grams of sample can be burnt in 20 to 30 minutes. Although the technique will be applicable to many types of sulphur combustion apparatus, the details given below refer to the Shell-Braun apparatus.

APPARATUS

Fig. 1 is a diagrammatical representation of the gas flow system, which is rendered independent of room air impurities by a precombustion section. This consists of a precombustion furnace (300 mm long, 28 mm bore), which bears a quartz tube (600 mm long and 23 mm outside diameter) filled with coarse quartz chips, leaning against a constriction at one side and kept in place by a wad of quartz wool. The electric furnace shall be of sufficient capacity to maintain temperatures of 800 to 1000° C when air at a rate of 500 l/h is passed through the apparatus for about 60 minutes. The entrance side of the precombustion tube is fitted to the scrubbers via a spherical joint 18/9 and 8 turns of Pyrex 12 mm tubing, the final connection being made by rubber tubing, glass to glass.

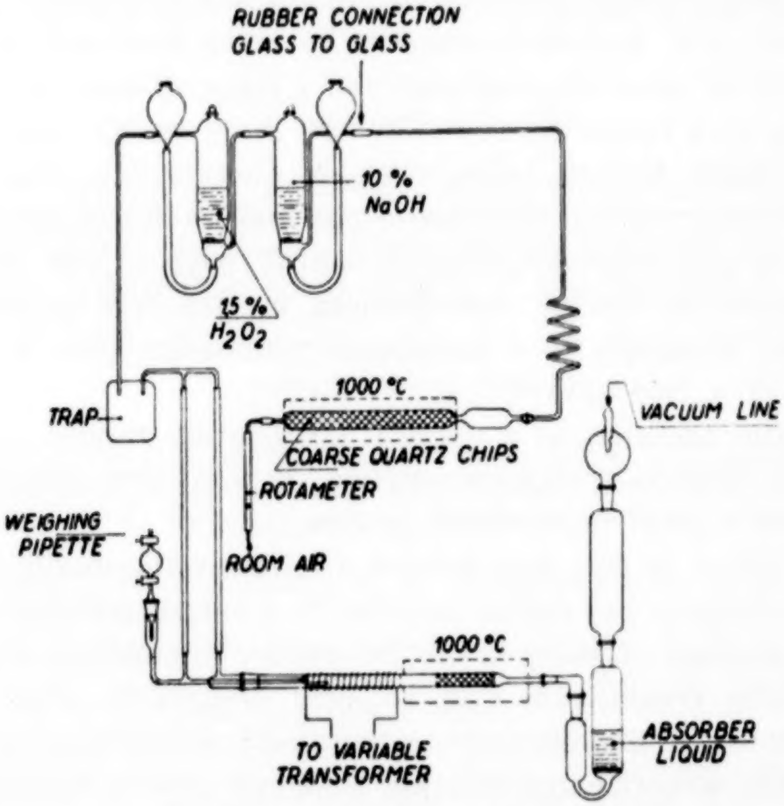
RUBBER CONNECTION GLASS TO GLASS
10 % NaOH
15 % H_2O_2
1000 °C
TRAP
COARSE QUARTZ CHIPS
VACUUM LINE
ROTAMETER
WEIGHING PIPETTE
ROOM AIR
1000 °C
TO VARIABLE TRANSFORMER
ABSORBER LIQUID

Fig. 1. Assembly of apparatus.

The dimensions of the combustion tube used by us are those of an earlier model than described by PETERS *et al.* The tube's sample part is provided with a wire coil heater for evaporation of the dropping sample. Details of the quartz tube and wire coil are given in Fig. 2. Fig. 3 shows the complete sample feed system. The position of the injector tip, ending just before the first windings of the wire coil, is rather critical. A roll of platinum gauze (5 mm long), installed against the first bored disc in the combustion tube, suppresses tendencies to backfiring. Constructional details concerning the weighing pipette and sample

References p. 65.

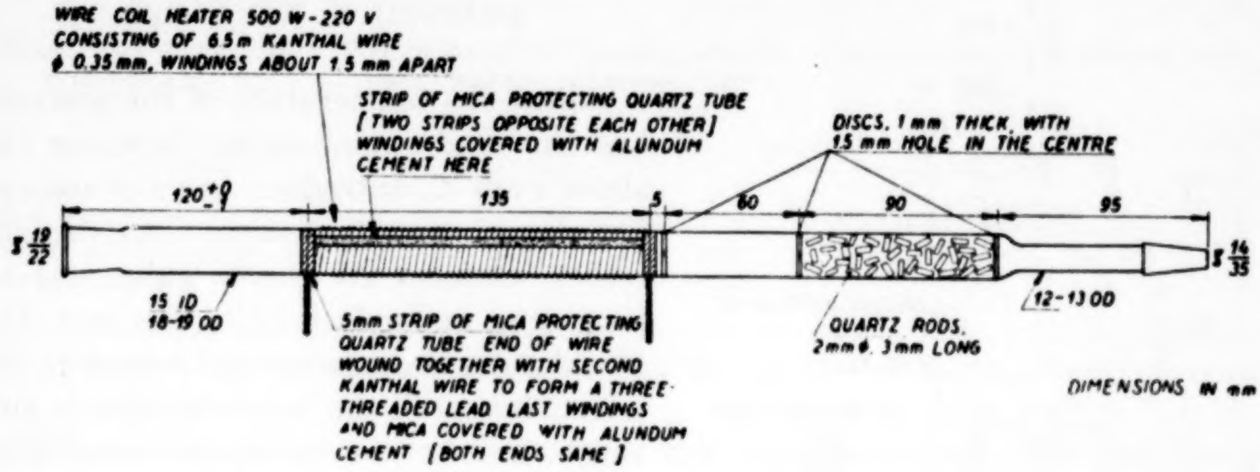
WIRE COIL HEATER 500 W - 220 V
CONSISTING OF 6.5 m KANTHAL WIRE
ϕ 0.35 mm, WINDINGS ABOUT 1.5 mm APART
STRIP OF MICA PROTECTING QUARTZ TUBE
[TWO STRIPS OPPOSITE EACH OTHER]
WINDINGS COVERED WITH ALUNDUM
CEMENT HERE
DISCS, 1 mm THICK, WITH
1.5 mm HOLE IN THE CENTRE
120 +0 -1
135
5
80
90
95
₮ 19/22
₮ 14/35
15 ID
18-19 OD
5mm STRIP OF MICA PROTECTING
QUARTZ TUBE END OF WIRE
WOUND TOGETHER WITH SECOND
KANTHAL WIRE TO FORM A THREE-
THREADED LEAD LAST WINDINGS
AND MICA COVERED WITH ALUNDUM
CEMENT [BOTH ENDS SAME]
QUARTZ RODS,
2mm ϕ, 3mm LONG
12-13 OD
DIMENSIONS IN mm

Fig. 2. Quartz combustion tube with wire coil heater.

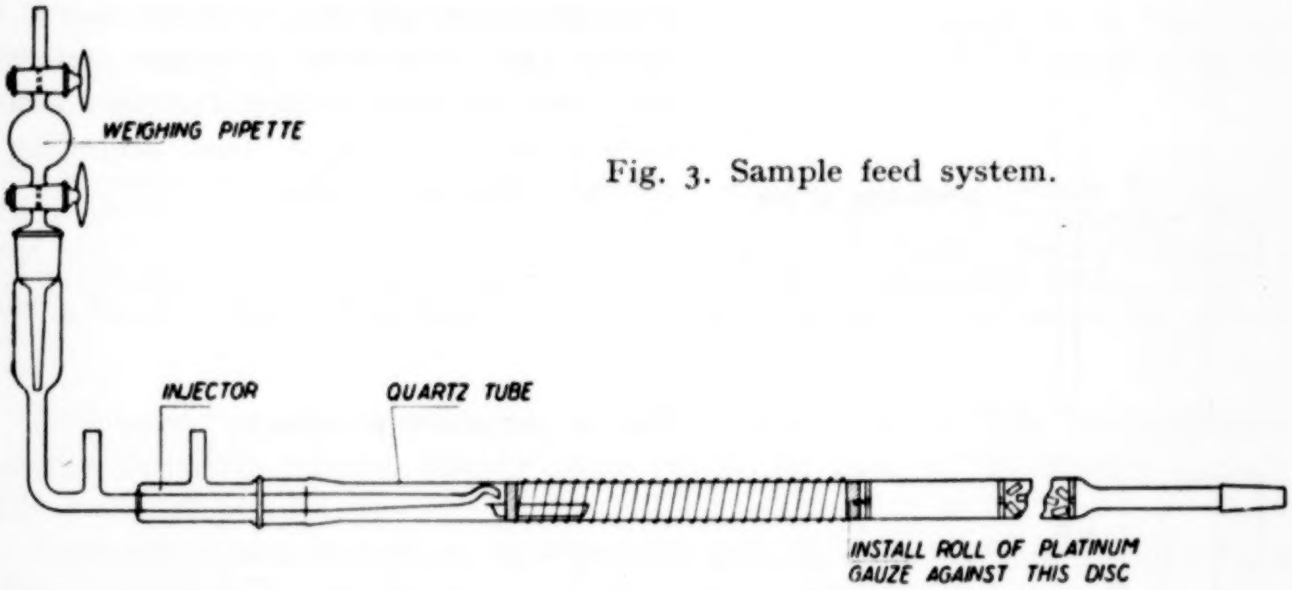
WEIGHING PIPETTE
INJECTOR
QUARTZ TUBE
INSTALL ROLL OF PLATINUM
GAUZE AGAINST THIS DISC

Fig. 3. Sample feed system.

injector are given in Figs. 4 and 5. Air is introduced in the combustion tube through two inlets; a primary air stream serves the purpose of transporting the dropping sample and a secondary stream supplies additional air required for complete combustion of the sample vapours. The separate air rates need not be controlled. One absorber combined with a foam trap is used instead of the original double absorption system[5], the resistance of which was too high for the required high air rate (450 l/h). Nevertheless, this single absorber proved quite effective in catching sulphur oxides and halogens in the low concentrations considered.

In assembling the apparatus care should be taken to have the entrance side of the combustion tube about 5 cm higher than the exit side so as to ensure smooth sample flow. The combustion tube is positioned in such a way that its first bored disc (the one which supports the platinum gauze) is flush with or not more than 10 mm outside the end of the electric furnace. A porcelain combustion boat (Coors No. 2) is placed in such a position in the coil-covered vaporization section that drops leaving the injector just fall into the boat.

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COMBUSTION PROCEDURE

Adjust the temperature of the precombustion and combustion furnaces to about 1100° C. Introduce 40 ml of absorption liquid (see discussion) into the absorber, connect to quartz tube and to foam trap and splash bulb. Connect the air inlets to the injector and attach to the quartz tube. Fill the weighing pipette and weigh. Connect to the injector and draw air through the apparatus at a rate of 450 l/h. The temperature of the combustion furnace will drop to about 1000° C. Check the connection between quartz tube and absorber. Adjust the wire coil section and the sample feed according to the following scheme:

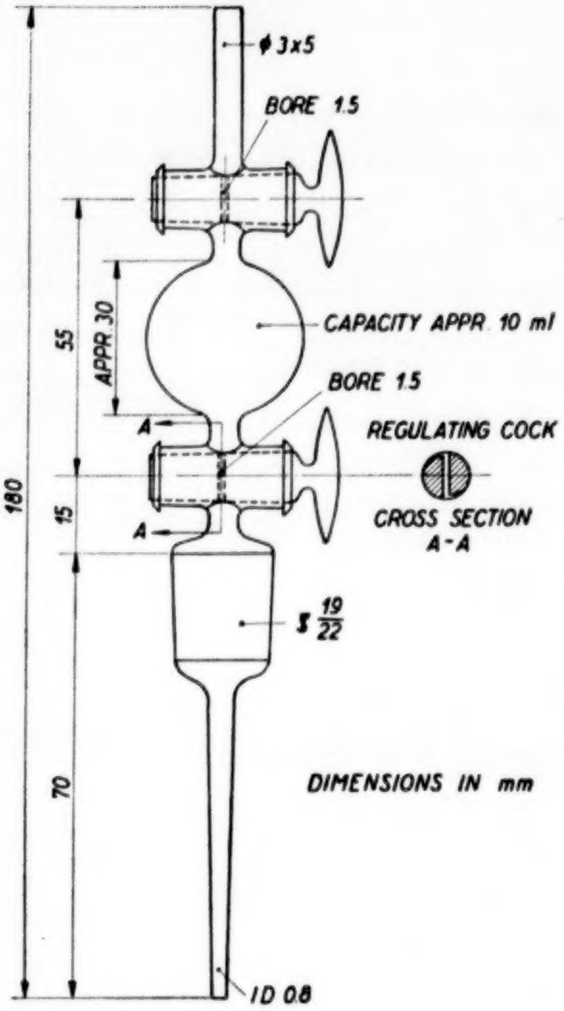
ϕ 3x5
BORE 1.5
CAPACITY APPR 10 ml
BORE 1.5
REGULATING COCK
CROSS SECTION A-A
A
A
180
55
APPR 30
15
70
$ 19/22
DIMENSIONS IN mm
ID 0.8

Fig. 4. Weighing pipette.

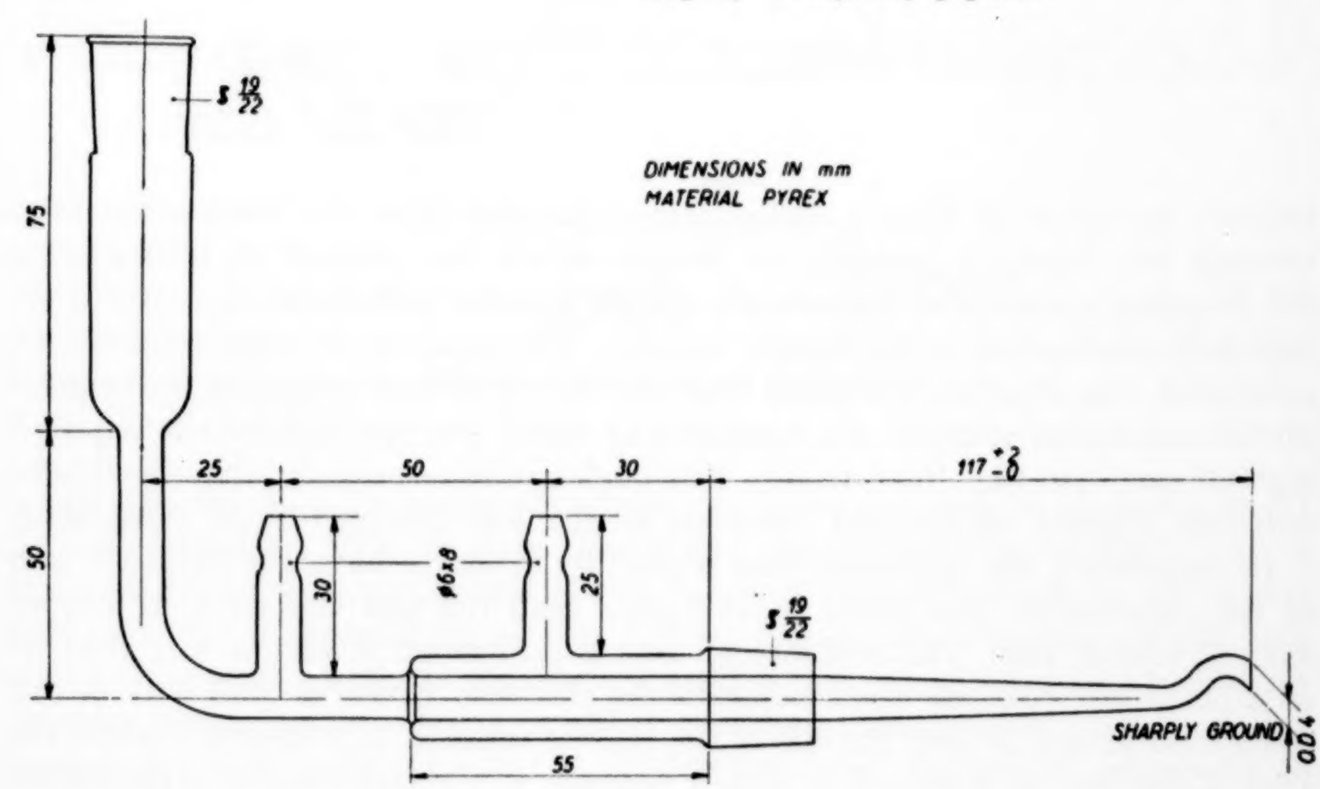
$ 19/22
DIMENSIONS IN mm
MATERIAL PYREX
75
50
25
50
30
117 +2 -0
30
ϕ6x8
25
$ 19/22
55
SHARPLY GROUND
0.04

Fig. 5. Injector.

Volatility of product comparable to	Apply to wire coil, Volts	Temp. inside wire coil*) °C	Approximate dropping rate
light gasoline	110	about 100	1 drop every 2 sec.
heavy gasoline/gas oil	170	,, 250	1 ,, ,, 3 ,,
lubricating oil	220	,, 500	1 ,, ,, 5 ,,

*) Measured under working conditions in the middle of the combustion boat.

With viscous samples, *start* the sample feed at a lower rate than the above one, thus allowing the inlet tube to be completely wetted with sample. This prevents the sample from being uncontrollably blown into the combustion zone. Control the dropping rate constantly. Decrease the power supply to the combustion section to such an extent that, combined with the heat liberated during combustion, a temperature close to 1000° C is maintained.

Temperature record from a thermocouple which is located outside the quartz tube gives only a rough estimation of the temperature actually existing inside the quartz tube. Experienced operators, therefore, will obtain a better impression of the temperature by observing the "colour" of the combustion section than by using thermocouples. Frequent overheating results in rapid breakage of the quartz tube.

As soon as a satisfactory quantity of sample has been burnt close the stopcocks of the weighing pipette. (Never allow the liquid level in the pipette to pass the lower stopcock.)

Continue suction at the same rate until the liquid is removed from the inlet tube (see discussion). Gradually heat the wire coil to full capacity in order to burn any residual liquid in the boat. Decrease the air rate in the case of a carbonaceous residue in order to obtain a higher temperature in the wire coil section. Persistent carbon deposits may require a shift of the boat into the hottest part of the section. Turn off the vacuum and rapidly disconnect the absorber from the quartz tube. Reweigh the weighing pipette and prepare the absorber solution for the final titration, gravimetric or turbidimetric step.

DISCUSSION

The optimum quantity of sample to be burnt is 5 grams. In cases where more sample is required it is advisable to add some fresh solution to the absorber between times in order to compensate for evaporation losses. The analytical finish of the absorber solution will depend on the character of the sample and on the amount of element present. The most rapid finish is allowed in the acidimetric sulphur determination where the absorber liquid is titrated in the same vessel with $0.05N$ sodium hydroxide solution using methyl red as the indicator. Satisfactory determinations have been made in this way of sulphur contents down to 0.003 per cent. sulphur using a 5-gram sample. When acid-forming elements other than sulphur are present, *e.g.* halogens and/or nitrogen, a gravimetric finish should be followed. A turbidimetric finish[10] will allow the determination of less than 0.003 per cent. sulphur using a 5-gram sample intake. 40 ml of a 3 per cent. hydrogen peroxide solution are a satisfactory absorber charge for sulphur determinations.

For halogen determinations the absorber is charged with 30 ml of a 3 per cent. hydrogen peroxide solution and 10 ml of a 2 per cent. sodium carbonate solution. Many halogen titration techniques can be followed in the final step. We followed a micropotentiometric finish[4] using $0.02N$ silver nitrate solution and chlorine contents down to 0.005 per cent. could be determined with reasonable accuracy, employing sample intakes of 5 grams.

It is advisable to renew daily the scrubber solutions in the air purification train. It has been found now and then that freshly prepared ASTM lamp sulphur absorbers show a persistent alkaline reaction which arrives from the sintered disc. Steam treatment is therefore recommended when the object is to use such absorbers in acidimetric sulphur determinations.

Viscous products are not completely removed from the inlet tube after stopping the sample feed. Depending on the desired accuracy this retained portion of sample may be removed by heating with a small sharp flame (utmost care is required in this case in order to avoid uncontrolled spattering into the combustion zone which results in incomplete combustion and soot formation) or may be neglected since the amount is actually small, *i.e.* of the order of 100 mg, and hence has only little effect on the results.

Inorganic residues left in the combustion section may contain some sulphate or halide and, depending on the desired accuracy, this can be washed from the boat and the tube in the case of halide or gravimetric (turbidimetric) sulphur finishes.

The connection between the quartz tube and absorber is made with the aid of conical joints. Considerable care is necessary in handling this connection due to the fact that a Pyrex female joint covers a quartz male joint. For this reason it is necessary to check the connection some time after a combustion has been started, *i.e.* when the female pyrex joint has expanded, in order to avoid leakages. It is likewise necessary to disconnect the absorber from the quartz tube as soon as the combustion procedure is completed in order to avoid sticking. Spherical joints as recommended in newer models of the apparatus will require less care in this respect. Their use was not investigated by us, but the very high temperatures which develop in the considered area using the present combustion technique suggest a necessary elongation of the quartz tube for reasons explained elsewhere[5].

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SUMMARY

A rapid combustion technique for the determination of small amounts of sulphur and halogens in organic liquids is described. The technique, in the first instance, refers to the Shell-Braun quartz tube combustion unit and offers an appreciable extension of the working area of this apparatus.

RÉSUMÉ

Une méthode rapide de combustion a été décrite pour déterminer de faibles quantités de soufre et d'halogènes dans des liquides organiques. La méthode se rattache principalement à l'appareil à tube de quartz ,,Shell-Braun'' et offre une extension appréciable de son applicabilité.

ZUSAMMENFASSUNG

Ein schnelles Verbrennungsverfahren zur Bestimmung von kleinen Mengen Schwefel und Halogene in organischen Flüssigkeiten wird beschrieben. Das Verfahren bezieht sich an erster Stelle auf das Shell-Braun Quartzrohr-Verbrennungsapparat und bietet eine erhebliche Erweiterung seines Anwendungsgebietes.

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AN IMPROVEMENT ON WRIGHT'S METHOD FOR THE MICRO-DETERMINATION OF MOLECULAR WEIGHTS

by

C. J. VAN NIEUWENBURG AND J. W. L. VAN LIGTEN

Laboratory of Microanalysis of the Technical University, Delft (Netherlands)

BARGER's well-known method for the determination of molecular weights by means of "isothermal distillation" is based on the principle that drops of solutions of two different solutes in the same solvent are of the same molecular strength when these drops are in equilibrium with each other. It has been carried out in a great many different ways, for instance, lately by NIEDERL *et al.*[1].

With all these modifications we meet the serious and often unsurmountable difficulty that equilibrium is only reached after a very long time, because the diffusion of the vapour is extremely slow, especially in capillary tubes, which are generally used.

In 1948 WRIGHT[2] suggested a new way of carrying it out. The underlying idea was fundamentally sound. In order to accelerate the diffusion process it is necessary to offer the vapour a short and broad way to travel. So he completely did away with the capillary tubes and replaced them by two filterpapers, soaked with the solutions, and placed opposite to and near each other. However in our opinion some details of his method of carrying out the quite sound principle are less recommendable, at least for a true micro-style of work. The aluminium boxes in which he puts the filterpapers are quite heavy, about 50 g. That is far too heavy for sensitive micro-balances which, on the other hand, must be used when one intends to weigh in the box itself minute amounts of substance with a reasonable accuracy. Indeed WRIGHT himself states that the weighing problem caused him a great deal of trouble, although he used as much as 10 mg of substance.

After a number of unsuccessful trials we came to the following procedure which gave us complete satisfaction.

We insert our filterpaper discs of 27 mm diameter into separate, light, aluminium, internally grooved rings, weighing not more than about 2 g, including the hooks for suspending them. Then both rings with paper discs in them are weighed, suspended on a sensitive torsion balance (0-25 or 0-50 mg), with an identical ring and paper as a counterweight. We note the readings of the torsion balance in tenths of a milligram. Then we bring the rings on to an automatic micro-

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balance, weigh them to six decimal places and weigh on them $\frac{1}{2}$-$1\frac{1}{2}$ mg of each of the two substances, one with a known and one with an unknown molecular weight. Then we add to both paper discs a sufficient amount of an appropriate solvent, say 20-30 mg, from a syringe. It is not necessary to know exactly how much. Both rings are rapidly packed into a closely fitting aluminium box (see Fig. 1), this box is closed with a rubber band around the rim, and stored for some time, varying from some hours to two days at a temperature of 20-30° C in a desiccator with the same solvent on a wad of cottonwool at the bottom of it.

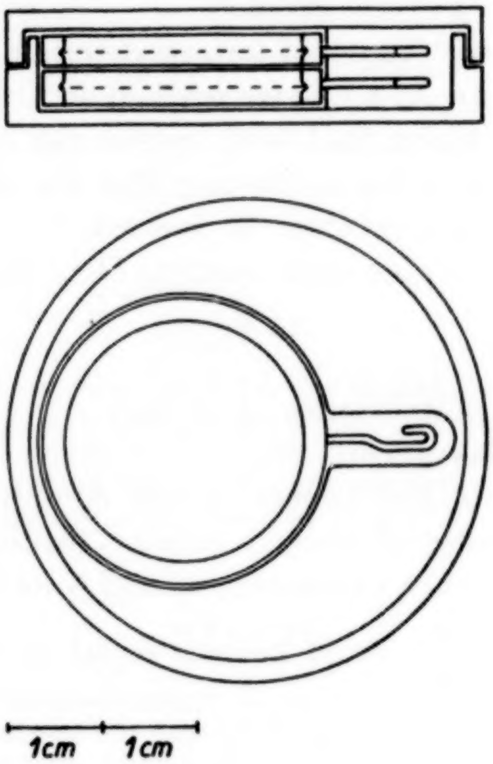

Fig. 1

Then the box is opened and both rings are weighed again on the same torsion balance, the rings now suspended in an atmosphere saturated with the vapour of the solvent. The difference in readings of the torsion balance (minus the weight of the substance) gives us the amount of solvent on each paper and all the necessary data for the calculation of the unknown molecular weight.

In order to prevent a loss of vapour along the lid of the box, notwithstanding the rubber band, it is desirable to put some grease on the rim, not the usual fatty kind which absorbs organic vapours, but for instance the grease which is obtained by bringing amylum into boiling glycerol.

Whereas WRIGHT used ethanol as a solvent (B.P. 78°), we prefer less volatile solvents, such as water (B.P. 100°), monochlorobenzene (B.P. 132°), *n*-butanol (B.P. 117°), ethylenechlorhydrin (B.P. 129°), xylene (B.P. 134-138°) and even aniline (B.P. 184°), although with the latter a slightly raised storing temperature,

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30-35° for two days, is desirable. As a rule the weighing difficulties become less as the boiling point of the solvent is higher, without seriously increasing the time necessary for reaching equilibrium. It is of course necessary that the solvent is able to dissolve a sufficient amount of the substance under investigation (5-10%), but moreover it is essential that it dissolves the substance rapidly so as to get an even distribution of the solution over the filterpaper.

As a rule, one day at room temperature, about 20°, is quite sufficient for reaching equilibrium. For security two days might be advisable. If the aluminium boxes are well fitting and greased, it is not strictly necessary to keep them in a desiccator filled with the solvent vapour.

The actual amount of work required for one determination can easily be done in three-quarters of an hour. As a rule we reached an accuracy well within 10%, often within 5%. It is striking that with xylene the accuracy is less. We are inclined to believe that this is due to the fact that the xylene we used was not a pure, single substance, but a mixture of isomers.

In the following table we give some results. They are expressed in values of $\frac{a}{MG}$, in which

a = weight of substance ($\frac{1}{2}$-$1\frac{1}{2}$ mg)
M = molecular weight
G = weight of the solvent in the equilibrium state
(= increase of torsion balance reading minus a)

It is evident that, whatever the values of a, M and G for the two substances under comparison, the quotient $\frac{a}{MG}$ must become equal in the course of time.

Solvent: *water*	quotient $\frac{a}{MG}$	
Citric acid and tartaric acid	100.8	and 98.0
Oxalic acid and urea	79.9	76.3
Citric acid and tartaric acid	21.9	20.3
Oxalic acid and citric acid	117.5	123
Solvent: *monochlorobenzene*		
Fluorene and benzil	34.2	31.4
Fluorene and tribromophenol	22.8	23.9
Fluorene and benzil	25.2	25.9
Fluorene and tribromophenol	18.8	19.9
Benzil and tribromophenol	26.7	29.3
Pyramidon and benzil	19.7	20.4
p-Chloronitrobenzene and *p*-chloronitrobenzene	87	89
Solvent: *n-butanol*		
Benzoic acid and citric acid	17.5	14.1
Pyramidon and quinine	21.4	22.6
Pyramidon and quinine	29.5	30.3
Dibromocinnamoic acid and tribromophenol	54.5	53.3
Tribromophenol and *o*-chlorobenzoic acid	27.7	28.4

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Solvent: *ethylene chlorhydrin*		
Tribromophenol and chlorohydroquinone	15.2	17.3
Tribromophenol and *o*-chlorobenzoic acid	74.5	69.4
Solvent: *aniline*		
Benzophenone and phenanthrene (96 h. at 30°)	18.8	17.7
Benzophenone and phenanthrene (48 h. at 30°)	108.2	108.3
Benzophenone and benzil (48 h. at 30°)	20.1	21.2
Benzophenone and benzil (48 h. at 30°)	29.3	28.0
Benzophenone and benzil (66 h. at 30°)	16.4	15.3
Solvent: *xylene*		
Azobenzene and phenanthrene (3 h. at 30°)	30.5	28.0
same sample after 24 h. at 20-25°	41.5	35.2
Azobenzene and fluorene (3 h. at 30°)	44.7	51.5

SUMMARY

An improvement of WRIGHT's method for the determination of molecular weights is described, in which the filterpapers, carrying the solutions, are handled and weighed in light aluminium rings, and equilibrium is reached inside a closely fitting aluminium box. There is a wide choice of appropriate solvents with boiling points ranging from 100-184°. The accuracy reached is 5-10%. The amount of substance required is about 1 mg.

RÉSUMÉ

Nous décrivons un perfectionnement de la méthode de WRIGHT pour la détermination des poids moléculaires. Les papiers-filtre portant les solutions sont manipulés et pesés dans des anneaux en aluminium; l'équilibre est atteint dans une boîte bien fermée, également en aluminium. On a le choix entre un grand nombre de solvants à points d'ébullition variant de 100 à 184°. La précision est de 5 à 10%. La quantité de substance nécessaire est environ 1 mg.

ZUSAMMENFASSUNG

Es wird eine Verbesserung beschrieben der WRIGHT'schen Methode für die Molekulargewichtsbestimmung. Die Filterpapierscheibschen welche die Lösungen tragen werden gefasst und gewogen in leichte Aluminiumringe; das Gleichgewicht wird ebenfalls in einer gut verschlossenen Aluminiumdose erreicht. Man hat die Wahl zwischen verschiedenen Lösungsmitteln mit Siedepünkten von 100-184°. Die erreichte Genauigkeit beträgt 5-10%. Die benötigte Substanzmenge beträgt rund 1 mg.

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L'HYGROPHOTOGRAPHIE, NOUVELLE MÉTHODE D'INVESTIGATION; PRINCIPE ET APPLICATIONS

par

JOSEPH SIVADJIAN

Institut Pasteur, Paris (France)

L'hygrophotographie est l'art d'obtenir des images avec l'action combinée de la lumière et de l'humidité, sur une couche sensible, comme la photographie est l'art d'obtenir des images grâce à l'action exclusive de la lumière.

On connaît des sels métalliques dont la couleur change en présence de l'humidité, le plus connu de ces sels étant le chlorure de cobalt, de même qu'on connaît aussi des sels métalliques, le nitrate et les halogénures d'argent en particulier, dont la coloration change sous l'action de la lumière. Mais on ne connaissait jusqu'ici aucun composé pouvant changer de coloration sous l'action de la lumière d'abord et de l'humidité ensuite.

Or, nous avons montré que dans certaines conditions, que nous avons décrites avec précision, on pouvait préparer sur place, dans l'épaisseur même des émulsions photographiques, un sel complexe d'iodure double d'argent et de mercure, ayant ces propriétés[1,2].

Lorsqu'on expose une plaque ainsi obtenue à la lumière solaire directe ou même diffuse, mais suffisamment intense, elle change de couleur en prenant une teinte noir violacé. On obtient un résultat analogue, mais avec plus de difficulté, lorsqu'on l'expose à une source de lumière artificielle intense, à celle d'une lampe à 100 bougies, par exemple.

En conservant la plaque exposée dans un endroit obscur pendant une durée qui peut varier, suivant l'intensité de l'impression, de deux à plusieurs jours, la nouvelle coloration disparaît et la plaque reprend progressivement sa couleur primitive. Si, au lieu de conserver la plaque impressionnée dans un endroit obscur, on la plonge dans une cuvette remplie d'eau, l'image disparaît instantanément ou bien elle s'affaiblit considérablement, ce qui contribue à abréger la durée de sa disparition.

La plaque non exposée, qui est jaune, peut donc servir en photographie pour la reproduction de clichés ou d'épreuves sur papier et, à ce titre, elle peut rendre

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des services dans les travaux photomécaniques ou d'agrandissements. La plaque exposée et noircie sous l'action de la lumière, comme elle reprend sa coloration jaune primitive sous l'influence de l'eau à l'état de traces, constitue par contre un réactif extrêmement sensible pour l'eau et pour l'humidité et, à ce point de vue, elle se montre bien supérieure aux réactifs habituels et en particulier au chlorure de cobalt. Ces plaques présentent de plus, vis-à-vis de ces réactifs, un avantage sérieux, parce qu'elles permettent de fixer définitivement, par tirage sur papier photographique, et de rendre ainsi tangibles, les résultats obtenus.

C'est ainsi que, lorsque nous appliquons sur la peau humaine une plaque hygrophotographique préalablement noircie par exposition à la lumière, nous remarquons, après quelques minutes de contact, l'apparition sur la plaque, de nombreux points jaunes correspondant aux endroits de la surface cutanée qui sont le siège d'un dégagement de la vapeur d'eau. Chez les enfants, ce dégagement de la vapeur, ou perspiration insensible, étant particulièrement active, si l'on applique la main de l'enfant sur une de ces plaques préparées comme nous venons de dire, en quelques secondes, la main se dessine sur la plaque d'une manière particulièrement frappante, en reproduisant exactement les striations de la peau (Fig. 1).

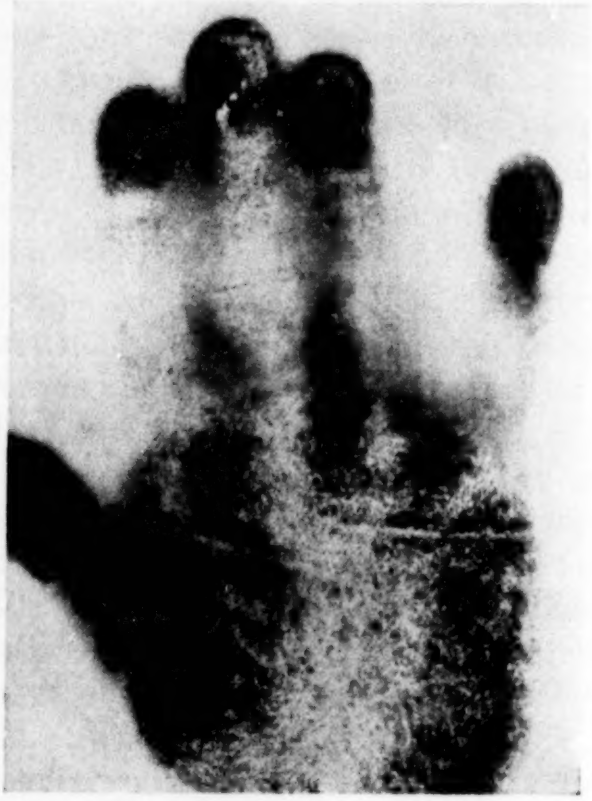

Fig. 1. La perspiration insensible de la main d'une fillette de 6 ans. 2 min d'exposition.

Si, à l'aide de pinces en bois, l'on fixe sur le pavillon de l'oreille du lapin la plaque hygrophotographique, l'on constate que celle-ci commence à se décolorer à partir de la base de l'oreille et que cette décoloration s'étend progressivement vers les autres régions de la plaque. Si l'on injecte alors à l'animal un produit vasodilatateur, la perspiration augmente d'une façon considérable, ce que l'on constate par l'extension importante de la partie décolorée de la plaque[3].

Lorsque nous appliquons la main sur une pellicule hygrophotographique, la perspiration insensible arrive à y imprimer une image de celle-ci tellement fidèle qu'on l'aurait pu confondre avec une image photographique réelle et sur laquelle on voit cependant, groupés dans certaines régions, des points noirs correspondant à l'activité des glandes. Si l'on pose la main sur la pellicule, après l'avoir chauffée d'abord sur une plaque métallique bien chaude, l'image hygrophotogra-

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phique se renforce davantage et l'on y voit les glandes sudoripares en nombre bien plus considérable. Quand on pose les extrémités des doigts, à l'exclusion du pouce, sur la plaque en donnant à la main une inclinaison de 45° sur celle-ci, et le pouce étant bien dégagée, afin d'éviter la formation d'un espace clos à l'arrière, on voit les empreintes des doigts s'inscrire normalement sur la plaque. Mais, en même temps, derrière ces empreintes, se dessine une „ombre" qui, suivant les conditions de l'expérience, peut atteindre jusqu'à un cm de longueur et qui est uniquement due à la perspiration insensible (Fig. 2). Si, au lieu d'appuyer la main sur la plaque, on la maintient horizontalement au-dessus de celle-ci, sur une hauteur de 10 mm au maximum, on voit également „l'ombre" se projeter sur la plaque et les contours très nets de cette „ombre" indiquent clairement que la vapeur dégagée, dont elle provient, n'est pas le résultat d'une simple diffusion lente, mais qu'elle doit être attribuée à une sorte de rayonnement, à un jet, en rapport évidemment avec le rayonnement calorifique cutané et lié par conséquent à la vie active des tissus sous-jacents[4].

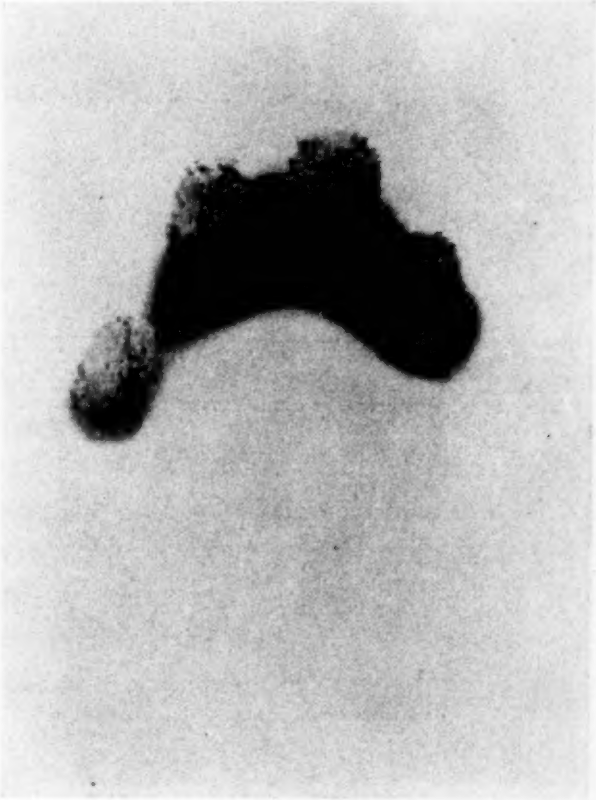

Fig. 2

L'étude de la perspiration insensible était faite jusqu'ici uniquement à l'aide de balances sensibles avec lesquelles on déterminait, soit la perte de poids par le sujet soumis à l'étude, soit l'augmentation du poids d'une certaine quantité de chlorure de calcium anhydre ou de tout autre produit hygroscopique servant à fixer la vapeur d'eau dégagée.

On voit que la méthode n'avait fait guère de progrès depuis 1614, date à laquelle Sanctorius publia pour la première fois, ses observations sur la perte de poids par le corps humain à l'aide d'une grande balance de sa construction.

Par contre, on a pu mettre au point des méthodes assez variées pour pouvoir enregistrer et étudier la secrétion sudorale, méthodes qui cependant restent très loin, quant à la sensibilité, vis-à-vis de la méthode hygrophotographique. Les plus employés de ces procédés sont: le papier iodoamidonné de MINOR[5], modifié par RANDALL[6], qui a pu mettre ainsi individuellement en évidence les glandes sudoripares de la patte du rat et de la peau humaine. THAYSEN, SCHWARTZ ET DOLE[7] préparent un papier iodoamidonné en faisant diffuser lentement par sublimation de l'iode dans l'épaisseur d'un papier imprégné d'amidon. HERRMANN, PROSE ET SULZBERGER[8] se sont servis du papier filtre recouvert d'une poudre composée de

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bromophénol bleu, de carbonate de sodium, d'amidon et de la gomme adragante. ANDERSON[9], FOWLE, LEGAULT DELLUVA ET GEORG[10] ont employé le papier au chlorure de cobalt, pour la mise en évidence et le dosage de la perspiration insensible et de la transpiration. GUTTMANN[11] a préconisé l'emploi de la quinizarine, tandis que SILVERMAN ET POWELL[12] ont pu rendre la transpiration visible à l'aide d'une réaction basée sur la formation d'encre lorsqu'un sel de fer vient au contact de l'acide tannique en présence de l'eau. MANUILA ET ISLER[13] appliquent sur la peau une bande adhésive recouverte d'une poudre composée d'un mélange de ferrocyanure de potassium et de sulfate de fer. En présence de l'eau, ces deux substances réagissent l'une sur l'autre en donnant du bleu de Prusse.

La mesure de la quantité d'eau dégagée par les plantes se faisait également jusqu'ici en se servant d'un potomètre ou d'une balance sensible. On avait aussi proposé l'emploi du papier au chlorure de cobalt[14] ou du papier à la cellophane[15].

Mais on peut aussi étudier indirectement les variations de la transpiration en déterminant les modifications de l'ouverture des stomates à l'aide d'appareils souvent encombrants et compliqués ou de techniques délicates, comme la méthode d'infiltration de MOLISCH[16].

Or, nous avons pu montrer que notre méthode hygrophotographique nous donne ici également un moyen extrêmement simple et rapide qui permet d'étudier la transpiration des plantes et ses variations avec une très grande sensibilité. Elle donne de plus la possibilité de faire l'étude topographique de cette transpiration, en mettant en évidence les parties de la surface foliaire où l'élimination de la vapeur d'eau est la plus intense[17,18].

L'étude de la transpiration des feuilles à l'aide de ces plaques a lieu de la manière suivante: les plaques préalablement exposées et noircies étant placées dans le cadre d'un châssis-presse, on applique la feuille, détachée ou non, contre la gélatine et on maintient serrées l'une contre l'autre les deux surfaces en contact, au moyen de la planchette brisée à charnières et des deux lames de ressort qui servent à immobiliser la planchette. Après quelques minutes de contact, on voit par transparence les contours de la feuille se dessiner sur la plaque sous l'influence de la vapeur d'eau dégagée par la transpiration. On retire alors la feuille et, en effectuant un tirage sur papier au bromure rapide, on obtient une image fidèle de la feuille, reproduite uniquement par l'eau de transpiration.

Si l'on veut étudier comparativement la transpiration de deux feuilles d'espèces ou de conditions différentes ou sur les deux faces de la feuille d'une même espèce, on applique, côte à côte, sur la même plaque, ces deux feuilles d'espèces différentes ou deux feuilles de la même espèce, mais chacune par une face différente.

On sait que les stomates se ferment à l'obscurité. Lorsque, après avoir recouvert pendant 24 heures les deux faces sur une moitié d'une feuille relativement jeune de *Pelargonium zonale* sur pied, au moyen d'un morceau de papier noir, tout en laissant l'autre moitié à la lumière, nous détachons cette feuille et l'appliquons sur la plaque hygrophotographique, nous constatons que l'impression de l'image ne se

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produit que sur la partie de la plaque qui se trouve en face de la moitié non recouverte de la feuille. La partie cachée laisse la plaque absolument intacte. Nous obtenons un résultat analogue lorsque nous recouvrons de papier noir l'une des folioles de *Fragaria vesca*. Cette foliole impressionne alors la plaque beaucoup plus faiblement que les deux autres folioles qui sont restées librement à la lumière (Fig. 3). Lorsque nous appliquons, dans le châssis-presse, une feuille panachée sur une plaque hygrophotographique, nous constatons que, sous l'action de la transpiration, qui est plus active dans les parties vertes que dans les régions étiolées, l'image hygrophotographique dessinée sur la plaque reproduit exactement les contours des parties vertes, les plages jaunes ne donnant aucune impression sur la plaque. Ce phénomène est absolument remarquable avec les feuilles dont la transpiration est active, telles que celles *d'Acer Negundo* (Fig. 4 et 5), *d'Abutilon Savitzii*. L'examen de ces images montre donc le rôle joué par la chlorophylle qui intervient activement dans la transpiration en favorisant le dégagement de la vapeur d'eau par les feuilles[19].

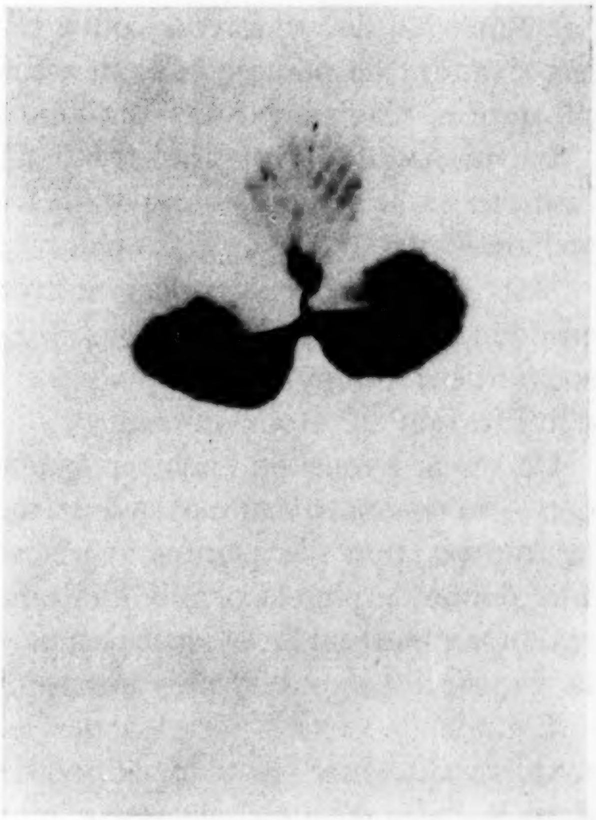

Fig. 3

La méthode hygrophotographique est susceptible aussi de rendre de grands services en météorologie, dans l'étude des précipitations atmosphériques, de la constitution des nuages et des brouillards, de même que pour la connaissance de la composition physique des brouillards artificiels et des aérosols employés dans l'industrie, dans la médecine et ailleurs.

La mesure du nombre et de la grosseur de gouttes de pluie et la découverte de la loi de la répartition des gouttes de différentes grosseurs dans une précipitation atmosphérique ont fait, depuis longtemps, l'objet de nombreuses études, à cause de la grande importance de la connaissance de ces éléments au point de vue de la genèse et de la formation des pluies.

Mais, ces dernières années, la distribution de la grosseur des gouttelettes dans la pluie a acquis un intérêt tout particulier à la suite de l'emploi du Radar pour la localisation des précipitations et pour le radio-guidage. L'écho du Radar reçu à partir de la précipitation est en effet extrêmement sensible à la grosseur des gouttelettes[20].

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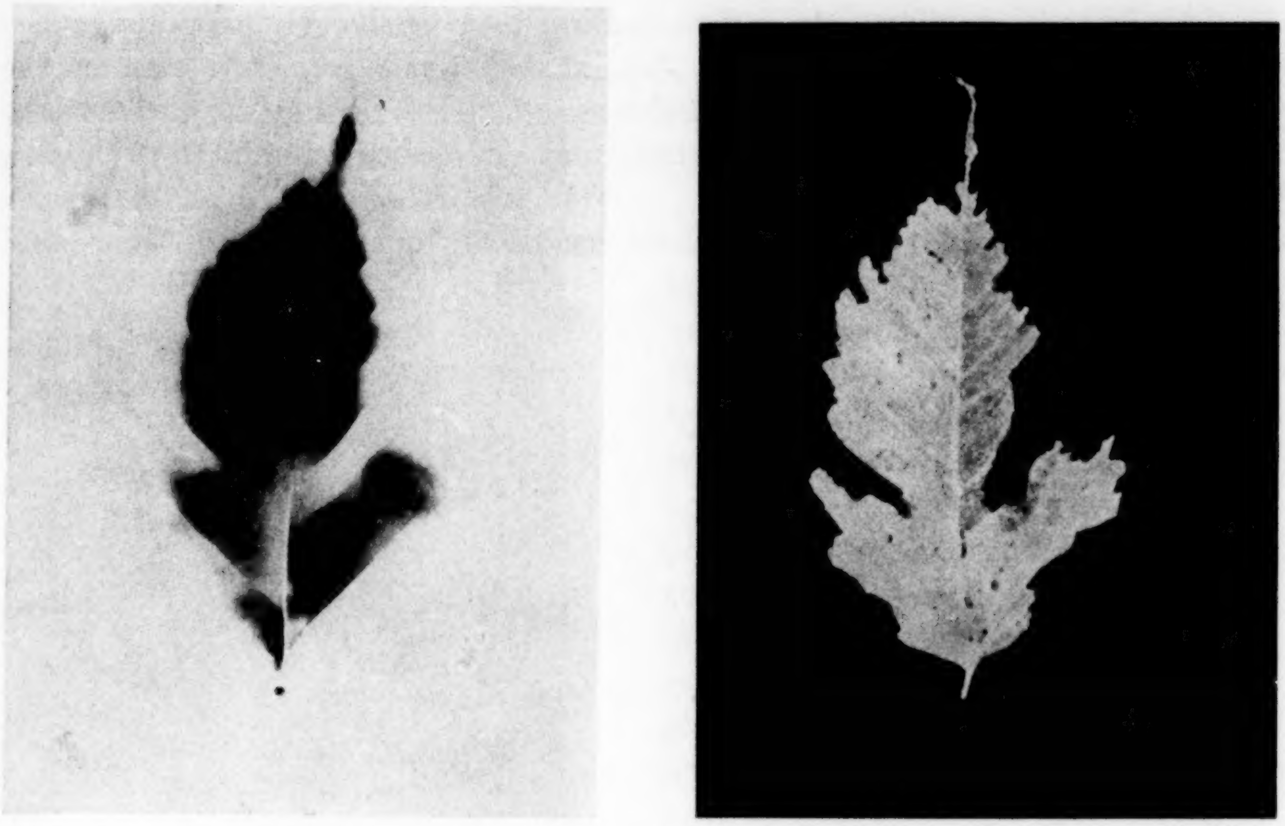

Fig. 4 et 5. Foliole d'Acer Negundo à feuilles panachées.
La Fig. 4 représente l'hygrophotographie reproduisant la partie verte de la foliole qui figure en blanc sur la photographie de la Fig. 5 de la même foliole, prise simplement par transparence.

C'est WIESNER[21] qui, le premier, s'est intéressé en 1895 à l'enregistrement et à la mesure de la grosseur des gouttes de pluie en se servant pour cela du papier filtre saupoudré d'une matière colorante pulvérisée et soluble, comme la rhodamine.

PAUTHENIER ET BRUN[22] ont amélioré cette méthode en remplaçant le papier filtre par du papier photographique brillant à grain très fin, sur lequel a été écrasé, par frottement, une poudre fine de bleu de méthylène. Une goutte d'eau arrivant sur le papier laisse une tache circulaire bleu clair, visible au microscope dans le cas d'une petite goutte. Ces auteurs ont remplacé par la suite le papier photographique coloré par une lame de verre sur laquelle on a placé une goutte de liquide non miscible à l'eau, tel que l'huile de paraffine. Cette technique s'inspire de celle de HAUSSER ET STROBL[24] qui exposent dans le courant de brouillard une lamelle de verre recouverte d'une mince couche d'huile de ricin. HOUGHTON ET RADFORD[25] ont remplacé l'huile de ricin par une couche uniforme de vaseline blanche sur plaquette de verre, qui a l'avantage d'éviter les inconvénients du glissement de l'huile le long de la plaque. Mais ces méthodes basées sur l'emploi des huiles sont loin de donner un ordre exact du nombre de particules contenues dans un ml d'aérosol[26] et elles donnent une loi de répartition statistique fausse, même pour les brouillards à grosses gouttes et des vitesses relatives assez fortes[27].

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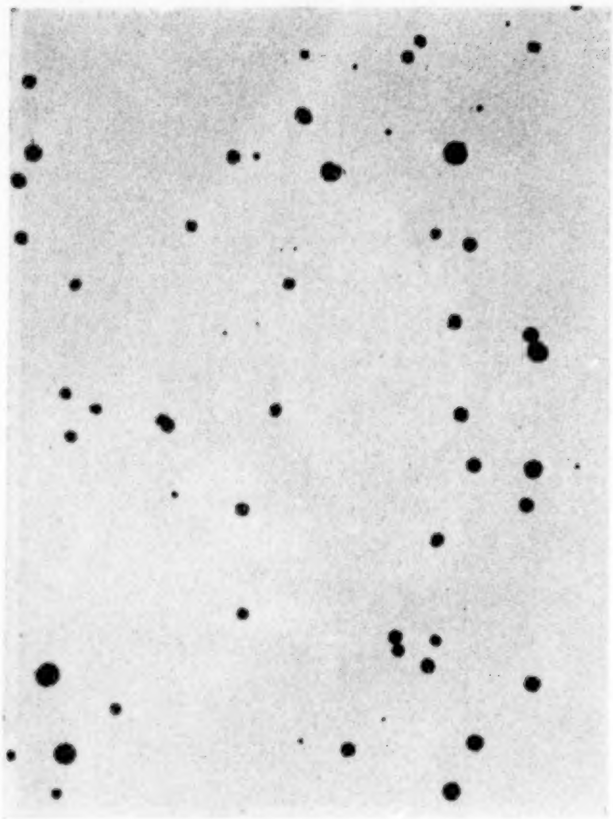

Fig. 6. Pluie du 15 Janvier 1952, à 11 h 35.

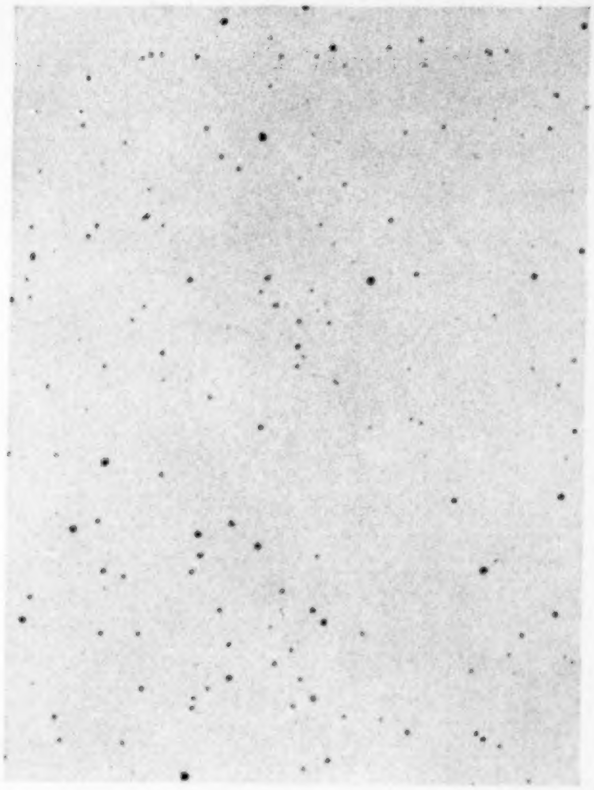

Fig. 7. Pluie du 11 Fevrier 1952, à 10 h 30.

DESSENS a proposé de se servir des fils d'araignées du genre *Aranea*, fils dont le diamètre est de l'ordre du micron, comme moyen de captation mécanique des gouttelettes de brouillard[28,29], tandis que BRUN, DEMON ET VASSEUR[27] ont réalisé à leur tour un réseau très serré de fils très fins de plexigum ayant un micron de diamètre et permettant une captation mécanique excellente[30]. BENTHLEY[31] reçoit les gouttes de pluie sur une couche de 25 mm d'épaisseur de farine très finement divisée et il détermine le diamètre des petites sphères formées par l'agglomération de la farine ainsi mouillée au contact des gouttelettes.

Les météorologistes anglais emploient un instrument appelé Aircraft Impactor qui est constitué essentiellement d'une plaque de verre couverte soit d'une couche uniforme d'huile, soit d'oxyde de magnésie, sur laquelle les gouttellettes forment des cratères[32], instrument dont le principe est indiqué par DIEM en 1942[33].

Or, nous avons montré[34] que nos plaques hygrophotographiques qui sont d'un maniement très simple et extrêmement rapide, permettent l'enregistrement instantané et direct des plus fines gouttelettes aqueuses à leur point d'impact, en donnant ainsi le moyen de suivre la variation de l'aspect de la pluie au cours d'une précipitation et d'en faire l'étude topographique, d'après les différentes grosseurs des gouttelettes recueillies (Fig. 6 et 7).

Bibliographie p. 78/79.

En appliquant en outre, avec précaution nos plaques hygrophotographiques sur les toiles *d'Aranea* chargées de la rosée matinale ou de gouttelettes de pluie, nous en avons pu obtenir des images grandeur naturelle, sur lesquelles il nous a été possible de mesurer la grosseur des gouttelettes dont les plus fines ont des diamètres variant de 20 à 30 microns (Fig. 8)[35].

On sait qu'il existe une différence fondamentale entre les fils qui forment les rayons d'une toile *d'Aranea* et ceux qui en forment la spirale, ces derniers étant enduits d'un produit visqueux, hygroscopique, alors que les premiers en sont dépourvus, différence qui apparaît nettement sur nos hygrophotographies. En effet, la rosée qui se condense sur place, ne se dépose pas sur la toile à l'état de gouttelettes, mais y est simplement absorbée par la matière gluante qui forme une suite de chapelets sur les fils transverseaux composant la spirale. Aussi, dans les hygrophotographies de la rosée matinale, les rayons de la toile ne sont-ils pas apparents, tandis que la pluie qui arrive au contact du filet à l'état de gouttelettes, s'y adhère aussi bien sur les rayons dépourvus de matière gluante que sur la spirale couverte de ce produit visqueux et, ainsi que la figure 8 le montre, l'image hygrophotographique reproduit aussi bien les uns que les autres[35].

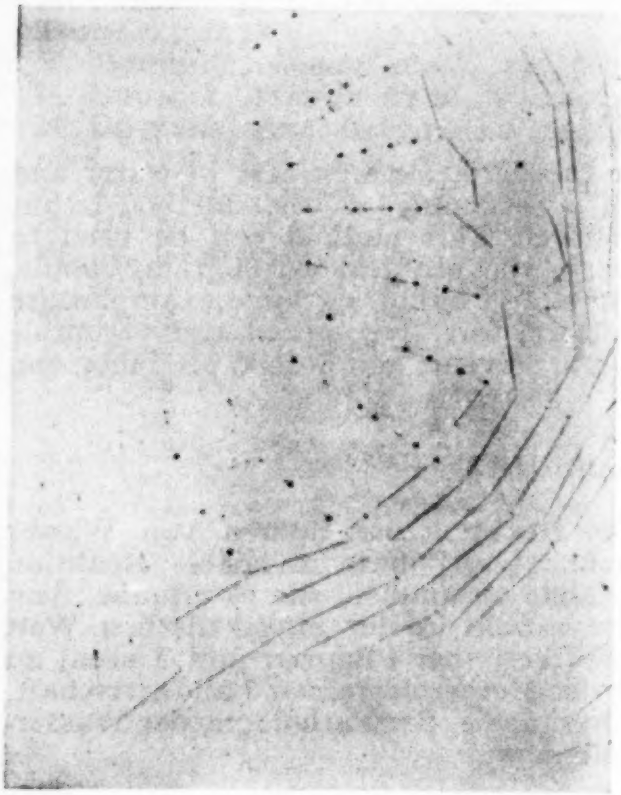

Fig. 8. Hygrophotographie de la toile d'Aranea, chargée de pluie. 5 Oct. 1952.

Enfin, nous ne citons encore que pour mémoire quelques expériences non encore tout à fait au point, relatives à l'emploi de la méthode hygrophotographique pour la détermination de la perméabilité à l'eau des terres arables et de l'humidité du sol, du point de fanaison, pour le dosage de l'eau dans les solvants et autres produits hydratés, etc.

Lorsque, à l'aide d'une micropipette, nous faisons tomber une petite goutte d'alcool absolu du commerce sur une feuille de papier filtre placée, bien serrée, entre la plaque hygrophotographique et une plaque de verre ordinaire transparente, nous voyons que l'alcool, ne pouvant pas s'évaporer rapidement, s'étale librement par adsorption, dans l'épaisseur du papier filtre. La très faible quantité d'humidité qui peut se trouver dans cette gouttelette, passe du papier dans la gélatine en donnant sur la plaque un anneau périphérique qui entoure un espace à peine décoloré.

Bibliographie p. 78/79.

RÉSUMÉ

L'auteur décrit une réaction photochimique de détection de l'eau à l'état de traces et à l'état de vapeur. Basée sur cette réaction qui est réversible, il met au point une technique, dite hygrophotographique, qui permet de suivre l'eau dans ses multiples pérégrinations aussi bien dans le monde physique (pluies, nuages, brouillards) que dans le monde organisé (chez les plantes et les animaux). Il donne des exemples d'applications à la météorologie, à l'agriculture, à la sylviculture, à la physiologie animale et à la physiologie végétale, à la pathologie, à l'analyse de l'eau dans les solvants et dans les produits alimentaires, etc.

SUMMARY

A photochemical reaction is described for the detection of traces of water and water vapour. Based on this reaction, which is reversible, another method is put forward, namely the hygrophotographic method. This method can be used to follow the numerous peregrinations of water in the physical world (rain, clouds, mists) as well as in the organic world (in plants and animals). Some examples are given of applications to meteorology, agriculture, forestry, animal and vegetable physiology, pathology, to the analysis of water in solvents and in food products, etc.

ZUSAMMENFASSUNG

Der Autor beschreibt eine photochemische Reaktion um Spuren von Wasser und um Wasserdampf zu bestimmen. Gegründet auf diese reversible Reaktion stellt er eine sog. hygrophotographische Methode zusammen, die es erlaubt, dem Wasser auf seinen vielfältigen Wanderungen sowohl in der physikalischen Welt (Regen, Wolken, Nebel), wie in der belebten Welt (bei Pflanzen und Tieren) zu folgen. Er gibt Beispiele zur Anwendung in der Meteorologie, der Landwirtschaft, der Forstwirtschaft, der Pflanzen- und Tierphysiologie, der Pathologie, der Wasseranalyse in Lösungsmitteln und Lebensmitteln usw.

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A COLORIMETRIC METHOD FOR THE DETERMINATION OF SILVER IN ORES

by

ANDERS RINGBOM AND ERKKI LINKO

Institute of Analytical and Inorganic Chemistry, Åbo Akademi, Åbo (Finland)

In 1928 FEIGL[1] introduced the reagent *p*-dimethylaminobenzalrhodanine for the detection of various noble metals, especially silver. Several attempts have since then been made to use this reagent for quantitative determinations. So SCHOONOVER[2], COAKILL[3] and SANDELL AND NEUMAYER[4] measured the color intensity of a colloid solution of the red silver salt. This method is sensitive but not very accurate, as ALLEN AND HOLLOWAY[5, 6] have shown. Moreover, large amounts of foreign ions interfere, and the method cannot be employed for the determination of silver in ores unless the silver is previously isolated (*cf.* SANDELL AND NEUMAYER[4]). RINGBOM[7] suggested another procedure. He precipitated the silver rhodanine complex from a dilute aqueous sulfuric acid medium, removed the coprecipitated reagent with boiling alcohol, dissolved the precipitate in alkaline potassium cyanide solution and measured the color intensity of the yellow solution. The silver concentration was calculated from the stoichiometric relation between rhodanine and silver.

In the following, experiments are described in which the method last mentioned was applied to the analysis of various argentiferous ores.

In order to eliminate the disturbing influence of gold the ore sample was dissolved in a pyrosulfate melt as in the determination of silver in metallic copper (RINGBOM[7]). Iron did not interfere if masked with phosphoric acid. In analyzing ores very rich in silver the results obtained were fairly satisfactory; but if the silver content was small too low values were obtained, which is probably due to the extremely high ionic strength resulting from the large amounts of ore and pyrosulfate required. It is obvious that the solubility of the silver salt will be considerable under such conditions.

SANDELL AND NEUMAYER[8, 9] have determined the dissociation constants of the ampholyte *p*-diethylaminobenzalrhodanine (HR) and the solubility product of the corresponding silver salt (AgR). They obtained the following values at an ionic strength of 0.05:

$$aH^+ \; [HR]/[HR{\cdot}H^+] = k_1 = 2{\cdot}10^{-4} \qquad (1)$$
$$aH^+ \; [R^-]/[HR] = k_2 = 7{\cdot}10^{-7} \qquad (2)$$
$$[Ag^+]\,[R^-] = 8{\cdot}10^{-19} \qquad (3)$$

For the solubility of HR the authors mentioned obtained the value $2.1{\cdot}10^{-7}$ moles per litre. Using these values of the constants the following relationship between the silver concentration and the acidity of a solution saturated with HR and AgR can be derived:

$$[Ag^+] = 10^{-5.3}\ aH$$

In other words, to maintain the silver ion concentration below 10^{-8} M (corresponding to *ca.* 1 μg Ag/l) it would be necessary to work at a pH above 2.7. It is likely that the equilibrium constants of the methylrhodanine do not differ very much from those of the ethylrhodanine.

These calculations refer, however, to solutions containing 20% alcohol. In water the solubility of AgR is probably lower. Moreover, the precipitating reagent HR will serve as a carrier for AgR. On the other hand, the solubility of the reagent is also lower in water, and at high ionic strengths the silver concentration in the solution will increase.

It is therefore obvious that the precipitation of very small amounts of silver will not be complete when large amounts of foreign electrolytes are present unless the solution is only slightly acid, neutral or alkaline. As many metals then will precipitate as hydroxides, it is necessary to mask these metals in a suitable way.

We have used ethylenediamine tetra-acetic acid EDTA (complexone, versene) for this purpose. This substance forms very strong complexes with most of the metals present in ores, *e.g.* Fe, Cu, Ni, Co, Zn, Al, Pb, but the silver complex seems to be rather weak. As, however, no data on the silver complex were found in the literature, we determined the value of its complexity constant, using the method previously suggested by SCHWARZENBACH[10].

Known amounts of silver nitrate were added to 50 ml samples of a solution $10^{-3}M$ in EDTA and $10^{-1}M$ in sodium nitrate. The samples were then potentiometrically titrated with $0.1N$ NaOH using a glass electrode.

TABLE I

$0.1N$ NaOH	C_{Ag}	pH	$[H_2Y^{-2}] + [HY^{-3}]$	$[AgY^{-3}]$	$[Ag^+]$	$[Y^{-4}]$	$\frac{[AgY^{-3}]}{[Ag^+]\,[Y^{-4}]} = K$
ml	$\times 10^4$		$\times 10^4$	$\times 10^4$	$\times 10^4$	$\times 10^8$	log K
1.69	10	6.50	4.77	5.23	4.77	5.7	7.28
1.42	10	6.00	7.42	2.58	7.42	1.7	7.31
1.75	20	6.50	3.96	6.04	14.0	4.8	6.96
1.48	20	6.00	6.60	3.40	16.6	1.5	7.13
					Average:		7.2

Table I shows the results of two titrations. The values in the first three columns are known or are measured; the values in the four following columns can be computed using the acid dissociation constants of EDTA (H_4Y): $pk_1 = 2.00$; $pk_2 = 2.67$; $pk_3 = 6.16$; $pk_4 = 10.26$.

Although the average pK value 7.2 lays no claim to a high degree of accuracy, this value implies that the silver complex is so weak that no appreciable amounts of the silver rhodanine will dissolve in a solution containing EDTA and saturated with the rhodanine reagent. Nevertheless the silver complex is so strong that silver chloride dissolves in an alkaline solution of EDTA.

The results of several analyses conducted in the presence of EDTA and different amounts of salts, acids and bases are given in Table II. Full details of the method recommended follow:

Reagents

p-*dimethylaminobenzalrhodanine, ca.* 20 mg (carefully weighed) of reagent, recrystallized from alcohol, in 100 ml of 0.01*N* sodium hydroxide. This is the standard solution. Small volumes of this solution are diluted with 0.001*N* sodium hydroxide in volumetric flasks. The aqueous, alkaline solutions are not stable over longer periods.

p-*dimethylaminobenzalrhodanine,* 0.02% in ethyl alcohol. This is the precipitating solution. The diethyl compound can be used as well.

Potassium cyanide, 0.5% in 0.001*N* sodium hydroxide.

Procedure

To 50 ml of solution containing not more than 70 μg of silver, add 3 ml of the alcoholic reagent solution. Allow the solution to stand in the dark for at least 2 hours. Filter through a glass filter crucible (Jena G4 or equivalent) and wash with a little water. Place the crucible in the beaker in which the precipitation was conducted and pour 40 ml of ethyl alcohol into the crucible and the beaker. Cover with a watch glass and boil very gently for 15 minutes. Remove the alcohol from the crucible by suction and wash the latter and the beaker with cold alcohol until the last washing is completely colorless. Empty and clean the suction flask.

Pour 5 ml of potassium cyanide solution into the beaker used for the precipitation and from the latter into the crucible, using a stirring rod to spread the solution over the walls of the vessels. Remove the solution from the crucible with suction and wash with a little water. Repeat the treatment with another 5 ml of cyanide solution. Transfer the solution from the suction flask to a 50 ml volumetric flask and dilute to the mark. Without undue delay, determine the transmittancy of the solution using a blue filter (460 mμ).

Prepare the calibration curve by measuring carefully 0.1 . . . . . 1 ml of the aqueous reagent solution, diluting to 50 ml with 0.001*N* sodium hydroxide,

TABLE II

No.	Added buffer substances M				pH	Added neutral salts M			Added heavy metal salts M		Added Na_2H_2Y M	% A	μg Ag obtained	μg Ag added
	NH_4^+	NH_3	NH_4Ac	HAc		NaCl	$NaNO_3$	K_2SO_4	Fe^{+3}	Cu^{+2}				
1	0.3	1	—	—	9.8	—	—	—	—	—	0.03	29.2	35.3	44.2
2	1	0.5	—	—	9.5	—	—	—	—	—	0.03	33.5	42.7	48.8
3	1	0.05	—	—	8.5	—	—	—	—	—	—	30.3	37.2	37.5
4	1	0.05	—	—	8.5	—	—	—	—	—	0.01	35.2	46.0	45.6
5	1	0.05	—	—	8.5	—	—	—	—	—	0.01	30.3	37.2	41.1
6	—	—	0.1	—	7.0	—	—	—	—	—	0.01	30.7	37.8	39.4
7	—	—	0.1	0.05	5.0	—	—	—	—	—	0.01	33.0	42.0	43.2
8	—	—	0.2	—	7.0	—	—	—	0.025	—	0.036	33.3	42.5	42.3
9	—	—	0.2	—	7.0	—	—	—	0.025	—	0.036	33.7	43.2	44.1
10	—	—	0.025	—	7.0	0.01	—	—	0.02	0.02	0.05	32.9	42.0	41.0
11	—	—	0.025	—	7.0	0.01	—	—	—	—	0.01	31.8	39.3	39.6
12	—	—	0.04	—	7.0	0.04	—	—	—	—	0.02	34.2	44.3	44.2
13	—	—	0.04	—	7.0	0.4	—	—	—	—	0.02	34.2	44.3	43.9
14	—	—	0.04	—	7.0	—	0.4	—	—	—	0.02	35.0	45.7	44.9
15	—	—	0.04	—	7.0	—	—	0.45	0.015	—	0.02	34.5	47.5	47.0
16	—	—	0.04	—	7.0	—	—	0.05	—	—	0.01	2.05	2.65	2.52

TABLE III

No.	Sample mg	Composition	$K_2S_2O_7$ g	Aliquot	% abs.	μg Ag	ppm Ag	
							obt.	from kupellation analysis
1	732	25% Fe, 21% Cu, 1.7 ppm Au	11	25/100	35.0	48.2	263	266
2	1,049.0	35% Fe, 19% Cu, 2.3 ppm Au	15	50/100	21.3	26.8	51.2	52
3	231.0	35% Fe, 15% Cu, 65.0 ppm Au	4	50/100	16.5	17.9	155	147
4	898.7	— ,, —	13	25/100	25.3	33.2	148	147
5	898.7	— ,, —	13	25/100	25.0	32.8	146	147
6	980	0.2 ppm Au	13	100/200	1.7	1.6	3.2	2
7	1,531	0.3 ppm Au	15	50/100	4.8	6.3	8.2	7

and determining the transmittancy. One part of the methyl rhodanine reagent corresponds to 0.4083 part of silver. Lambert-Beer's law is obeyed when sufficiently selective filter is used.

We have used a Lange photoelectric colorimeter and 50 ml cuvettes (thickness of solution = 15 mm). The blue filters used were not, however, monochromatic, and hence the calibration curve was not quite linear. As we had to change the lamp during our experiments, the silver values have been taken from two different calibration curves.

Except for the first two values, which apply to ammoniacal solutions, the agreement is fairly satisfactory. The errors in the ammoniacal solutions might be attributed to the formation of the silver ammonia complex. However, calculations based on equilibrium constants do not make this explanation likely. The errors are probably caused by the fact that the solubility of the reagent is rather high in alkaline solution. The reagent does not therefore serve as a carrier, whereas in neutral or slightly acid solution the precipitation of the reagent is almost quantitative. This carrier effect is probably the reason why very small amounts of silver — about 1 μg — can also be determined by the method described.

It will be noted that there is no interference by chlorides or nitrates. In this respect the new procedure is advantageous compared with the previously suggested procedure (RINGBOM[7]).

The method was then used to analyse various silvercontaining ores. The procedure was as follows:

Transfer a suitable sample — usually 0.5 to 1 g — to a fairly large silica or porcelain crucible. Add potassium pyrosulfate in an amount about 15-20 times that of the sample, heat the covered crucible cautiously, gradually increasing the flame, and finally heat for 10-15 minutes at red heat. After allowing the crucible to cool, place it in a beaker and add 50-100 ml of water. Heat until all the soluble matter has dissolved and transfer the solution and undissolved matter into a 100 ml (or larger) volumetric flask, and dilute to volume. When the insoluble matter has settled (preferably overnight), take a suitable aliquot with a pipette and dilute to *ca.* 100 ml. Add a volume of 0.2M disodiumethylenediamine tetraacetate (Complexone III) slightly in excess of the amount equivalent to the heavy metals present in the solution. Make the solution slightly alkaline with ammonia, add 3 ml of the alcoholic reagent solution and neutralize with acetic acid to pH 6-7 (*i.e.* until the reagent precipitates). Allow the solution to stand for 2 hours, and proceed according to the directions given above.

The experiments 4 and 5 were made in the presence of 100 mg lead added as nitrate.

The agreement is fairly satisfactory. It may be mentioned that palladium is probably the only metal that possibly could interfere.

SUMMARY

A procedure is given for the colorimetric determination of silver in ores by means of *p*-dimethylaminobenzalrhodanine. The silver complex is precipitated in approximately neutral solution and the coprecipitated reagent is removed by washing with alcohol. The precipitate is dissolved in potassium cyanide solution and the intensity of the yellow solution is measured.

Interfering metals are masked with ethylenediamine tetra-acetate. Chlorides and nitrates do not interfere.

The complexity constant of silver ethylenediamine tetra-acetate is determined to $10^{7.2}$.

RÉSUMÉ

On propose, pour le dosage de l'argent dans les minerais, une méthode colorimétrique, utilisant comme réactif la *p*-diméthylaminobenzylidène-rhodanine. Le sel d'argent est précipité, et le réactif entraîné est éliminé par l'alcool éthylique. Le précipité est dissous dans une solution aqueuse de cyanure de potassium, et l'intensité de la coloration jaune est mesurée.

Les métaux accompagnants sont masqués par une solution d'éthylènediaminotétracétate. Les chlorures et les nitrates ne gênent pas.

La constante de stabilité du complexe argent-éthylènediaminotétracétate est déterminée et l'on obtient la valeur $10^{7.2}$.

ZUSAMMENFASSUNG

Eine Methode wurde beschrieben, welche *p*-Dimethylaminobanzalrhodanin für die colorimetrische Bestimmung von Silber in Erzen verwendet. Das Silbersalz wird in beinahe neutraler Lösung ausgefällt, ausgefälltes Reagens durch Waschen mit Alkohol entfernt, der Niederschlag in einer Kaliumcyanidlösung gelöst und die Farbenintensität der erhaltenen gelben Lösung gemessen.

Anwesende Metallionen sind mit Äthylendiamintetra-acetat maskiert. Chloride und Nitrate stören die Bestimmung nicht.

Die Komplexkonstante von Silber-Äthylendiamintetra-acetat wurde zu $10^{7.2}$ bestimmt.

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PHOTOMETRIC DETERMINATION OF OSMIUM WITH THIOUREA AFTER EXTRACTION OF THE TETROXIDE

by

R. D. SAUERBRUNN* AND E. B. SANDELL

School of Chemistry, University of Minnesota, Minneapolis, Minn. (U.S.A.)

The usual way of separating osmium from other elements is by distillation of its tetroxide. An alternative method may be based on the extraction of the tetroxide from aqueous solution by carbon tetrachloride or chloroform. Data are presented here to show the usefulness of the extraction method in the range 5-1000γ Os. It appears to be equal, if not superior, to the distillation method in most respects for the isolation of microgram quantities of osmium. Its use is particularly advantageous when very small amounts of osmium are involved, because the final volume, in which the photometric determination is made, is readily restricted to 5 ml; the sensitivity, and therewith the precision, therefore is greater than in the distillation method in which the final volume is greater.

The partition coefficients, as determined by the writers at 25° C, for the two solvents mentioned are:

Ionic strength M	$[OsO_4]_{CCl_4}/[OsO_4]_{H_2O}$	$[OsO_4]_{CHCl_3}/[OsO_4]_{H_2O}$
0	13.0	19.1
1.0	14.8	—

Electrolytes increase the value of the partition coefficient by their salting-out effect on the non-polar osmium tetroxide in water. At the relatively low osmium concentrations dealt with in analysis, the partition coefficient is essentially independent of the osmium concentration. Taking 50 ml as a reasonable volume of the aqueous phase and 10 ml as that of each portion of the organic solvent for extraction, we obtain the following percentage recoveries of osmium for n extractions by applying the familiar relation $R(\%) = 100 \left\{ 1 - \dfrac{1}{\left(\dfrac{PV_o}{V_w} + 1\right)^n} \right\}$:

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* From a portion of the Ph. D. thesis of R. D. SAUERBRUNN, 1952.

No. of extractions	R, %	
	CCl_4 (P = 13.0)	$CHCl_3$ (P = 19.1)
1	72.2	79.3
2	92.3	95.7
3	97.9	99.1
4	99.4	99.8

Four extractions under these conditions are sufficient. In trace analysis, three extractions with chloroform will often suffice, and perhaps even two with the use of a correction for the unextracted osmium.

Determination of osmium in the combined organic solvent extracts is readily effected by shaking with a sulfuric acid solution of thiourea to give the red complex $Os(NH_2CSNH_2)_6^{+3}$ and obtaining the transmittancy of the aqueous phase.

Ruthenium (VIII) will accompany osmium in the extraction. The partition coefficient $[RuO_4]_{CCl_4}/[RuO_4]_{H_2O}$ has the value 59[1]. Since ruthenium gives a bluish color with thiourea and thus interferes in the photometric osmium determination, its extraction must be prevented. If osmium and ruthenium are both present in the +8 form (often the case after preliminary treatment of the sample), they can be reduced with a little ferrous iron[2]; addition of concentrated nitric acid to make its concentration about 5 M oxidizes osmium to the tetroxide at room temperature, while leaving ruthenium in the reduced form. Extraction then effects a sharp separation of the two elements.

Introduction of chloride in the preparation of the sample is to be avoided if possible, because it must be eliminated before osmium can be extracted. Chloroosmate ($OsCl_6^{-2}$) is not easily converted into the tetroxide by oxidizing agents, especially in the presence of excess chloride. If chloride must be introduced, as in the solution of meteoritic iron in hydrochloric acid, it may be removed by evaporation to fumes with sulfuric acid, at a temperature no higher than actually necessary, in the presence of a reducing agent such as ferrous iron to assure maintenance of osmium in the quadrivalent state.

Table I gives results obtained by the extraction method, according to the general directions below. A spectrophotometer with 1 cm absorption cells was used.

PROCEDURE

The volume of the solution (chloride-free) should be such that when ready for extraction it does not exceed approximately 50 ml. Preferably more than 5 γ Os should be present. If osmium is not in the octavalent form (as when ferrous salts are present), add 5 ml of 6 N sulfuric acid and 2.5 ml of 85 per cent. phosphoric

TABLE I

PHOTOMETRIC DETERMINATION OF OSMIUM AFTER EXTRACTION OF THE TETROXIDE

(50 ml aqueous solution extracted with four 10 ml portions of organic solvent)

No.[a]	Addition	Os taken	Os found	
		γ	CCl_4 extn. γ	$CHCl_3$ extn. γ
1		5.0	4.9	4.9
2		10.0	9.8	9.9
3		20.0	19.6	19.8
4		20.0	19.7	19.8
5		40.0	39.4	39.7
6		40.0	39.2	39.6
7		1160	1150	1150
8		1160	1140	1150
9	1 g Fe^{+3} (sulfate)	1160	1140	1150
10	1 g Fe^{+3} (sulfate)	1160	1130	1150
11	1 g Cu^{+2} (sulfate)	1160	1140	1150
12	1 g Cu^{+2}, 1 g Fe^{+3} (sulfates)	1160	1140	1150
13	100 γ Ru(III)	0.0	0.0	—
14	100 γ Ru(III)	5.0	4.8	—
15	100 γ Ru(III)	10.0	9.3	—
16	100 γ Ru(III)	10.0	10.0	—
17	100 γ Ru(III)	10.0	9.8	—
18	100 γ Ru(III)	10.0	10.0	—
19	100 γ Ru(III)	20.0	19.8	—
20	0.5 g Fe^{+2}, 0.5 g Cu^{+2}, 100 γ Ru(III)	5.0	4.8	—
21	0.5 g Fe^{+2}, 0.5 g Cu^{+2}, 100 γ Ru (III)	10.0	9.8	—
22	0.5 g Fe^{+2}, 0.5 g Cu^{+2}, 100 γ Ru(III)	20.0	19.8	—
23	0.5 g Fe^{+2}, 0.5 g Cu^{+2}, 1 mg Pd(II), 1 mg Pt(IV), 100 γ Ru(III)	0.0	0.0	—
24	0.5 g Fe^{+2}, 0.5 g Cu^{+2}, 1 mg Pd(II), 1 mg Pt(IV), 100 γ Ru(III)	10.0	10.0	—
25	1.0 g Fe, 100 γ Ru(III)	5.0	4.7	—
26	1.0 g Fe, 1 mg Pd(II), 1 mg Pt(IV), 100 γ Ru(III)	10.0	9.2	—
27	1.0 g Fe, 100 γ Ru(III)	20.0	18.6	—

[a] In Nos. 1-12, osmium was added as OsO_4 and extracted directly. In Nos. 13-24, the permanganate-ferrous ammonium sulfate-nitric acid treatment was applied before extraction; iron was present originally as ferrous salt, In Nos. 25-27, iron was added as the metal (ingot iron) and, after dissolving the $KMnO_4$-Fe^{+2}-HNO_3 treatment was applied.

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acid to approximately 25 ml of solution. Then add dropwise a 5 per cent. solution of potassium permanganate until a pink color appears. (If much ferrous iron is present the potassium permanganate may be added as finely ground solid to keep the volume of the solution as small as possible). Discharge the permanganate color with 25 mg of ferrous ammonium sulfate added as solid or in solution. If the color is not completely discharged add an equal amount of ferrous ammonium sulfate. The solution should be free from turbidity or insoluble material. Do not allow the solution to become warm during the oxidation, lest some osmium tetroxide be volatilized.

Transfer the solution to a separatory funnel, and add 15 ml of concentrated nitric acid (or enough to make its concentration 5 *M*). Cool the solution to 20-25° C, add 10 ml of reagent-quality chloroform (less preferably carbon tetrachloride), and shake vigorously for 2 minutes. Allow the phases to separate and deliver the chloroform layer into a dry glass-stoppered bottle or flask. Repeat the extraction with two or three 10 ml portions of chloroform, depending on the recovery desired (see table of recovery factors).

To the combined chloroform extracts add exactly 5 ml of 0.1 *M* thiourea in 1 *N* sulfuric acid (prepared fresh daily) and shake vigorously for 5 minutes (a mechanical shaker operating at $\sim$180 cycles per minute is conveniently used). Separate the phases and transfer the clear aqueous layer to an absorption cell (1 cm is satisfactory) and obtain the transmittancy at 480 mμ in a spectrophotometer or filter photometer. If the red color is strong, dilute the solution with water to an appropriate volume before reading.

Establish the standard curve by treating known amounts of osmium tetroxide in water with thiourea; the final concentration of the latter may be about 0.1 *M* in 1 *N* sulfuric acid, but the concentrations are not critical.

SUMMARY

A general method for the determination of 5-1000 γ of osmium involves extraction of osmium tetroxide with chloroform or carbon tetrachloride, followed by shaking the organic solvent with a sulfuric acid solution of thiourea to form red $Os(NH_2CSNH_2)_6^{+3}$, whose color intensity is measured photometrically. A sharp separation of osmium from ruthenium can be obtained by reducing Os(VIII) and Ru(VIII) with ferrous sulfate and then oxidizing Os(IV) to Os(VIII) with nitric acid; ruthenium remains reduced and is not extracted by chloroform or carbon tetrachloride.

RÉSUMÉ

Une méthode générale de dosage de l'osmium (5-1000 γ) est basée sur l'extraction du tétroxyde d'osmium par le chloroforme ou le tétrachlorure de carbone; on agite ensuite le solvant organique avec une solution sulfurique de thiourée; il y a alors formation du complexe rouge $Os(NH_2CSNH_2)_6^{+3}$ dont l'intensité de la coloration est mesurée par photométrie. On peut séparer l'osmium du ruthénium en réduisant Os(VIII) et Ru(VIII) par le sulfate de fer(II) et en oxydant ensuite Os(IV) en Os(VIII) par l'acide nitrique; le ruthénium reste à l'état réduit et n'est pas extrait par le chloroforme ou le tétrachlorure de carbone.

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ZUSAMMENFASSUNG

Eine allgemeine Methode zur Bestimmung von 5-1000 γ Osmium besteht aus der Extraktion von Osmiumtetraoxyd mit Chloroform oder Tetrachlorkohlenstoff und Schütteln des organischen Lösungsmittels mit einer schwefelsäuren Thioharnstofflösung um rotes $Os(NH_2CSNH_2)_6^{+3}$ zu bilden, dessen Farbstärke photometrisch gemessen wird. Eine scharfe Trennung des Osmiums vom Ruthenium kann durch Reduktion von Os(VIII) und Ru(VIII) mit Ferrosulfat und nachfolgender Oxydation des Os(IV) zu Os(VIII) mit salpetriger Säure erreicht werden. Ruthenium wird nicht oxydiert und wird nicht mit Chloroform oder Tetrachlorkohlenstoff extrahiert.

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THE POLAROGRAPHIC BEHAVIOUR OF SOME ELEMENTS IN CONCENTRATED CALCIUM CHLORIDE SOLUTION

III. THE POLAROGRAPHY OF COPPER, CADMIUM, IRON AND MANGANESE

by

G. F. REYNOLDS, H. I. SHALGOSKY AND T. J. WEBBER

Chemical Inspectorate, Ministry of Supply, Royal Arsenal, London (England)

INTRODUCTION

This paper discusses in detail the polarographic behaviour of Cu(II), Cd(II), Fe(III), and Mn(II) in $5M$ calcium chloride solution. The reason for such a study in this base electrolyte, and one method for its preparation, have already been given in a previous paper[1], in which the general difficulties inherent in the use of a medium of such high viscosity and low water free energy have also been described. The polarography of chromium, nickel and lead in this medium has also been previously discussed[2].

The work was carried out on a Randles type single-sweep cathode ray polarograph constructed in these laboratories[3,4] as this instrument is much more sensitive than conventional instruments and is much more rapid in operation. The essential differences between the results obtained by cathode ray methods and those of conventional polarography have already been discussed[1,4].

All potentials quoted in this paper are true half-wave potentials versus the normal hydrogen electrode (vs. N.H.E.) and the American sign convention has also been employed throughout. All pH values refer to solutions which have been diluted tenfold since, as already stated[1], direct pH determinations on $5M$ calcium chloride are almost meaningless.

THE POLAROGRAPHY OF COPPER

The electrochemical reduction of copper(II) takes place either as:

(a) $Cu(II) \rightarrow Cu$ . . . . 1.
or (b) $Cu(II) \rightarrow Cu(I)$ . . . . 2.
and $Cu(I) \rightarrow Cu$ . . . . 3.

Very little work on the reduction of Cu(II) in chloride solutions has been published, and it is difficult to predict whether (a) or (b) will be the mechanism of this reduction in 5*M* calcium chloride, as for this purpose it is necessary to know the relative tendencies for reductions 1 and 2 to occur. If all complexing is neglected, then the half-wave potential of reduction 1, represented by:

$$Cu \rightarrow Cu^{+2} + 2e^- \quad \ldots\ldots \quad 4.$$

is calculated to be —0.30 volts. The half-wave potential of reduction 2, represented by:

$$Cu^+ \rightarrow Cu^{+2} + 1e^- \quad \ldots\ldots \quad 5.$$

is calculated to be —0.05 volts. Since the potential of reduction 4 is 0.25 volts more negative than reduction 5, it would tend to occur much more readily.

However, solutions of 5*M* calcium chloride containing copper are yellow, indicating almost total complexing of the cupric ions. Cuprous ions, formed by reduction of the cupric, will also be complexed to at least $[CuCl_2]^-$.

Reductions 4 and 5 may be written more correctly therefore, as:

$$Cu + xCl^- \rightarrow Cu^{+2}\,(Cl^-)_x + 2e^- \quad \ldots\ldots \quad 6.$$

$$\text{and } CuCl_2^- + xCl^- \rightarrow Cu^{+2}\,(Cl^-)_x + 2Cl^- + 1e^- \quad \ldots\ldots \quad 7.$$

Due to the uncertain nature of the $Cu^{+2}\,(Cl^-)_x$ ion, it is not possible to calculate the exact shift in the positive direction which this stabilisation of the cupric ion will cause. It is likely, however, that this shift will be of a similar magnitude for each of the above mechanisms. Thus the difference between the half-wave potentials of reductions 6 and 7 will be of the same order as for the reductions 4 and 5 of the uncomplexed ions, *i.e.* 0.25 volts.

In the case of reduction 7, however, there should also be a shift of half-wave potential in the *negative* direction due to the unusual case of the reduced ion being complexed. The magnitude of this shift was calculated to be 0.5 volts and hence it is most probable that the shift could actually reverse the tendency for reduction 6 to occur about 0.25 volts more readily than reduction 7. Thus the reactions most likely to occur in 5*M* calcium chloride solution are 2 and 3, and two steps, each a one-electron change, should be observed when Cu(II) is reduced in this medium.

KHLOPIN[5] has reported a half-wave potential of +0.035 volts for Cu(II) in "30 per cent." calcium chloride, whilst we have found one wave (above zero applied volts) at +0.085 volts using 5*M* calcium chloride as base electrolyte. Calculations involving the Ilkovic equation indicate that the reduction is a one-electron change and this was confirmed by micro-coulometric analysis[6]. Since only one step is observed, reduction 3 must be that which is occurring and the electrode reaction will be:

$$Cu + 2Cl^- \rightarrow CuCl_2^- + 1e^-$$

The half-wave potential of this reduction in $5M$ calcium chloride is calculated from free energy data to be + 0.083 volts which agrees well with the observed value.

As would be expected from the solubility product of cupric hydroxide, no marked change in the peak height of the copper step was noted between pH 1 and 6. Small changes in step-height, such as those reported for lead[2], have not been looked for, but it is recommended that calibrations and determinations should be carried out within a small selected pH range if very accurate results are desired.

THE POLAROGRAPHY OF CADMIUM

In dilute potassium chloride solution, the reduction represented by the couple:

$$Cd \rightarrow Cd^{+2} + 2e^-$$

occurring at + 0.36 volts which is very close to the thermodynamically calculated value. KHLOPIN[5] has reported a value of + 0.42 volts for cadmium in "30 per cent." calcium chloride. We have found a value of + 0.56 volts using $5M$ calcium chloride which indicates a not entirely unexpected complexing of the cadmium in the strong chloride solution. Insufficient thermodynamic data is available, however, to enable a calculation of the particular ionic species reducing to be made.

Due to the high solubility product of cadmium hydroxide, the peakheight of the step due to cadmium hydroxide is proportional to its concentration in solutions up to a pH value of about 9. Serious interference is encountered due to the reductions of chromium and nickel unless the pH of the solution is sufficiently high to cause precipitation of these elements as hydroxides.

THE POLAROGRAPHY OF IRON

The presence of ferric iron in $5M$ calcium chloride solution gives rise to a reduction wave, the diffusion current and half-wave potential of which vary with pH. The wave observed is due to the reduction Fe(II) → Fe, the Fe(III) → Fe(II) change occurring at a lower potential, presumably below zero applied volts. When the pH of the solution was greater than about 5, no wave was observed, indicating the complete precipitation of an insoluble ferric compound. As the pH was decreased below 5, the concentration of the reducible ionic species (as indicated by the diffusion current) increased, probably due to the formation of some form of ferric-hydroxy-chloride complex ion. The half-wave potential consequently becomes more negative, as is usual for the reduction of an element not forming an amalgam at the electrode surface; the observed value fell from + 1.05 volts at pH 5 to +0.95 volts at pH 3.5. Below the latter pH, the discharge of hydrogen ion interfered with the iron wave. Thus only a strict pH control over a narrow range would enable this reduction to be used for the determination of iron, and it is not recommended for analytical purposes.

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THE POLAROGRAPHY OF MANGANESE

The reduction of manganese generally used for its polarographic determination is represented by the couple:

$$\mathrm{Mn} \rightarrow \mathrm{Mn}^{+2} + 2e^-$$

and the thermodynamically calculated half-wave potential for this reduction in 5*M* calcium chloride is +1.15 volts. The half-wave potential found was +1.20 volts which indicates that little complexing of the Mn^{+2} ion occurs.

In acid solutions interference can occur owing to the reductions of chromium, iron and nitrate ions, as well as from the discharge of hydrogen ions. The reduction wave due to the presence of nitrate was found to be disproportionately large and to occur at +1.30 volts; this wave has been reported by MEITES[7] to be due to a catalytic hydrogen reduction. Thus nitrate must be absent from solutions in which manganese is to be determined. The reduction Fe(II) → Fe and Cr(II) → Cr are best avoided by precipitation of the elements as hydroxides. Chromic hydroxide is known[2] to commence precipitating in 5*M* calcium chloride at a pH of approximately 3.5.

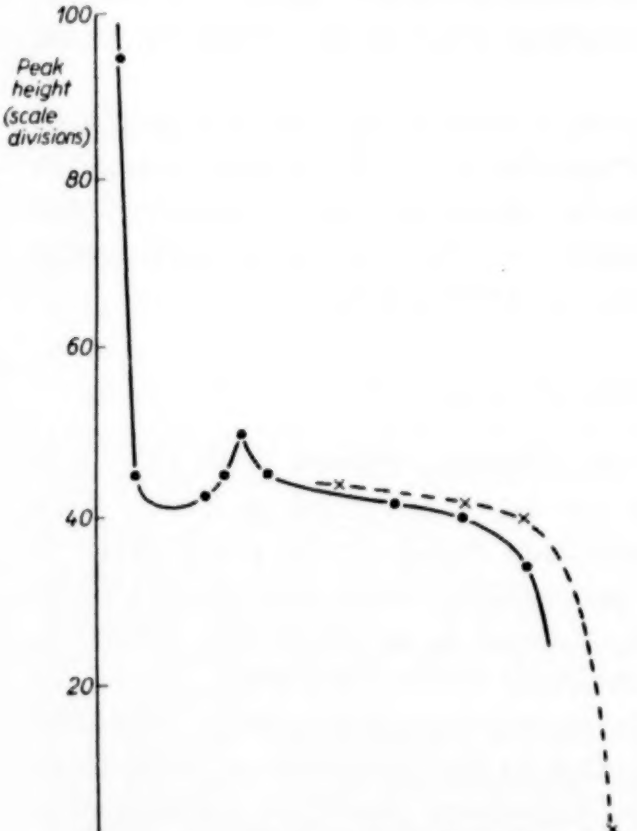

Fig. 1. Effect of pH on the manganese peak height
• 50 p.p.m. Mn in presence of 550 p.p.m. Fe^{+3}
× 50 p.p.m. Mn alone

However, the lower pH limit for the satisfactory polarography of manganese is governed by a combination of two reductions, both of which interfere with the manganese peak. The interfering waves are due to the reduction of ferrous iron and to the discharge of hydrogen. It was calculated that the latter would interfere at pH 3.7 and, in practice, interference was encountered at pH 3.5. The effect of varying pH on the peak height of a given concentration of manganese in the presence and absence of added iron is shown in Fig. 1. The interference of the hydrogen discharge mentioned above is indicated by the sharp rise in peak height at the extreme left of the curve.

The pH value at which precipitation of manganese hydroxide would begin to have a significant effect on the peak height was calculated to be 9. It can be seen, however, from the broken line in Fig. 1 that precipitation commences, in the absence of added iron, at pH 8.5. This discrepancy is probably due to the traces of iron in the materials used to prepare the calcium chloride solutions. The effect of the presence of significant quantities of iron is seen to slightly decrease the upper pH value for satisfactory polarography due, presumably, to the coprecipitation of manganese with ferric hydroxide.

The small peak which occurs at about pH 5 in Fig. 1 is caused by an enhancement of the manganese peakheight by the simultaneous discharge of ferrous ions at the electrode. These ferrous ions (*cf.* above) result from the previous reduction of some form of ferric complex more soluble than the hydroxide. Above pH 5, the amount of it in solution becomes negligible as indicated by the decreasing interference with the manganese peak height. At pH values below 5 the concentration of this iron complex increases, and there is the consequent displacement of the half-wave potential to a more negative value. The iron and manganese peaks therefore separate and the enhancement of the manganese peak decreases. This is shown by the left hand limb of the small peak in Fig. 1, which has been obtained from measurements of the peak height recognisably due to the reduction of manganese. It is thus seen that the most satisfactory pH range for the determination of manganese is about 5 to 7.5.

INTERFERENCES FOUND WITH THE COPPER, CADMIUM, IRON AND MANGANESE REDUCTIONS

No mutual interference of copper, cadmium and manganese can occur, but under certain conditions which have already been detailed, iron will interfere with the manganese determination. This interference is avoided by using a solution of pH greater than 5. Chromate ions will interfere with the copper determination and must be absent. Warming a slightly acid solution to which hydrogen peroxide has been added will ensure this. Excess hydrogen peroxide must be decomposed by thorough boiling before polarographing the solution. Cadmium, especially when very small amounts are present, may suffer interference from large amounts of nickel, even at pH 8.0. This interference is difficult to eliminate and will be dealt with fully in Part IV of this series of reports, together with details of the development of a method for the polarographic determination of trace impurities in calcium metal.

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References p. 96.

SUMMARY

This paper discusses in detail the polarography of copper, cadmium, iron and manganese in $5M$ calcium chloride. The conditions for polarography are laid down and the theoretical aspects of the results obtained with a single-sweep cathode ray polarograph are discussed. The mutual interference of the elements is detailed and recommendations for their determination in the presence of one another are presented.

RÉSUMÉ

Les auteurs exposent en détail la polarographie du cuivre, du cadmium, du fer et du manganèse, en solution dans le chlorure de calcium $5M$. Les conditions d'expérience sont données et les résultats obtenus avec le polarographe à rayon cathodique („single-sweep"), sont discutés du point de vue théorique. L'influence mutuelle de ces éléments est examinée, et une méthode est proposée pour les doser les uns en présence des autres.

ZUSAMMENFASSUNG

Die Arbeit bespricht eingehend die Polarographie von Kupfer, Cadmium, Eisen und Mangan in $5M$ Calciumchloridlösung. Die polarographischen Bedingungen werden festgelegt und die erhaltenen Ergebnisse der Kathodenstrahl — („single-sweep") — Polarographie werden vom theoretischen Gesichtspunkt aus besprochen. Die wechselseitige Störung dieser Elemente wird eingehend besprochen und eine Empfehlung zu ihrer Bestimmung in Gegenwart der anderen vorgeschlagen.

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8. Wertigkeiten sollten in der folgenden Weise A^{-n}, B^{+n} z.B. SO^{-2}, Fe^{+3} (nicht SO^{--}, SO'' oder SO^{2-} bzw. Fe^{+++}, $Fe^{\cdots}$ oder Fe^{3+}) angegeben werden.

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10. Die Autoren erhalten 25 Sonderdrucke ihrer Artikel unentgeltlich. Zusätzliche Exemplare können zu den Bedingungen, die auf den, den Autoren mit den Korrekturbogen zugehenden, Formularen angegeben sind, bestellt werden.

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THE DIELECTRIC CONSTANT AND SALT EFFECTS UPON THE ACID HYDROLYSIS OF METHYL PROPIONATE*

by

JAMES LEE HOCKERSMITH AND EDWARD S. AMIS

Chemistry Department, University of Arkansas, Fayetteville, Arkansas (U.S.A.)

A study of both the acid and basic hydrolysis of esters as a function of the dielectric constant of the solvent and of neutral salt concentration should be of interest in view of existing theories of rates of reactions between ions and dipolar molecules. Since esters are hydrolyzed by both hydronium and hydroxyl ions the theories of ion-dipolar reaction rates could be investigated with respect to both positive and negative ions reacting with an identical dipolar molecule under like conditions of concentrations of reactants, temperature, and dielectric constant of solvent.

EXPERIMENTAL

The bath thermometers were calibrated using a Bureau of Standards thermometer. The bath temperatures were held to within $\pm 0.02^\circ$ C.

A set of analytical weights was calibrated using Bureau of Standards weights.

All volumetric flasks, pipettes, and burets were calibrated. Glass stoppered Pyrex bottles, 500 ml, were used as reaction flasks.

Carbonate-free sodium hydroxide stock solutions were prepared as described by KOLTHOFF AND SANDELL[1]. Stock solutions of approximately $0.3N$ sodium hydroxide were prepared by diluting the one to one carbonate-free solution. These stock solutions were standardized against potassium acid phthalate and stored in paraffin-lined carboys equipped with ascarite tubes to protect the solutions from atmospheric carbon dioxide. The $0.0200N$ sodium hydroxide solutions used as a titrating agent were prepared in two liter batches at frequent intervals by dilution of the stock solutions.

A stock solution of hydrochloric acid was prepared by diluting C. P. concentrated (37%) acid. The stock solutions which were approximately $0.4500N$,

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* This work was done on a contract made by the Institute of Science and Technology of the University of Arkansas with the Office of Naval Research.

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were standardized against standard sodium hydroxide solutions. The 0.0200N HCl solutions used in all runs were prepared by dilution of this stock solution.

The acetone was purified by the method of ÅKERLÖF[2]. Acetone, EIMER AND AMEND tested, containing 14 ml of 85% phosphoric acid per liter, was distilled. The distillate was then dried over burnt powdered lime for twenty-four hours, poured off and redistilled, all but the fraction which came over between 54.6° and 54.8° C at a pressure of 727.5 mm mercury being rejected.

Methyl propionate, Eastman Kodak Company, was dried over calcium chloride for twenty-four hours and distilled. The fraction coming off between 77.20° and 77.35° C at a pressure of 723 mm mercury was collected. This corrected to atmospheric pressure using YOUNG'S[3] formula gives an average boiling point of 78.8. MUNCH[4] gives the boiling point of methyl propionate as 79.0° C. The refractive index of this fraction was found to be 1.3759 using sodium light at 23° C. MUNCH records an $n_D{}^{25}$ value of 1.3738 and AUWERS AND EISENLOHR[5] give the $n_D{}^{18.9}$ value of methyl propionate to be 1.37697. Our measured values of density were $d_4^{25.13} = 0.9066$ and $d_4^{45.48} = 0.8921$. AUWERS AND EISENLOHR record $d_4^{18.9}$ as 0.9038. MUNCH, however, gives d_4^{25} for methyl propionate to be 0.9107. From these data we believe our product to be quite pure.

A normal solution of sodium nitrate in distilled water was prepared from C. P. sodium nitrate. Necessary amounts of this stock salt solution were then added to the kinetic runs to give the desired ionic strength.

Analytical techniques were checked by duplicating a kinetic run whose reaction velocity constant has been established. The acid hydrolysis of ethyl acetate as reported by HARNED AND PFANSTIEL[6] was chosen for this purpose. Exact duplication of their experimental work gave very good checks of their reported velocity constants. This indicated that both reagents and technique were satisfactory. No experimental results were available concerning the acid hydrolysis of methyl propionate.

The purpose of this study was to determine the kinetics of the acid hydrolysis of methyl propionate under conditions of varying (1) ionic strength, and (2) dielectric constant. The procedure employed was as follows: The amount of stock HCl solution necessary to prepare 500 ml of a 0.0200N HCl solution was placed in a calibrated 500 ml volumetric flask and the necessary amount of 1.0000N $NaNO_3$ solution was placed in the volumetric flask to adjust the ionic strength to the desired value. The volumetric flask was then filled approximately three-quarters full with boiled distilled water, placed in a thermostat, and allowed to reach temperature equilibrium, after which the reaction was initiated by the addition of the necessary amount of methyl propionate, already at temperature equilibrium, to yield a 0.0100N ester solution. The volumetric flask was then filled to the mark with thermostated boiled distilled water, thoroughly shaken, and transferred to the pyrex reaction bottles. The initial time of mixing was noted and recorded. All runs were made in duplicate.

The reactions were followed by periodic withdrawals of 10.00 ml samples of the reacting mixture. The contents of the pipette were allowed to drain upon crushed ice (made from distilled water) in order to slow down the hydrolysis process. The cold samples, approximately 0.2° C, were titrated with $0.0100 N$ sodium hydroxide to a phenolphthalein end point. The reactions were followed until hydrolysis was approximately 70% complete when possible. A final titration was made after the reaction had ample time to reach completion — usually several days to a week.

Runs to test the dependence upon dielectric constant of the reaction were prepared in much the same manner as were the ionic strength runs. The ionic strength of these runs was constant (0.0200) and due only to the hydrochloric acid. Acetone was added in progressive amounts to lower the dielectric constant of the solution. After the reaction was initiated by the addition of methyl propionate samples were withdrawn periodically and placed in a flask containing crushed ice. These samples were then titrated with $0.0100 N$ sodium hydroxide using bromthymol blue indicator.

Plotting $-2.303 \log (C_{\infty} - C_t)$ versus time yields a straight line of slope k', as can be seen from integrating the equation for a first order rate without limits. Now C of the ester at time t equals $(C_{\infty} - C_t)$ where C_{∞} is the calculated concentration of propionic acid at infinite time and C_t is the concentration of the acid at time t. Hence

$$-2.303 \log (C_{\infty} - C_t) = k't + \text{constant} \quad \ldots\ldots\ldots \quad (1)$$

The values of k' recorded in the data were obtained from the slopes of the log concentrations versus time plots. This gave a more accurate value of k' than separate calculations of individual runs, using the equation integrated between limits.

The precision of the titrations and the agreement of the two methods of calculating k' are shown by the typical data of a run which gave $k' = 3.57 \pm 0.07$ by calculation using the form of the equation integrated between limits, and $k' = 3.54$ when the calculation was made using the slope of the log concentration versus time plots.

DIELECTRIC CONSTANT EFFECT

In Table I are recorded the kinetic data at constant acid and ester concentration and constant ionic strength. In these data the dielectric constant decreases with increasing weight per cent. acetone component of solvent. In addition to the specific velocity constant, k', the energies of activation, ΔE, and the Arrhenius frequency factors, B, are included in Table I. The energies and frequency factors were calculated from the k'/CH_2O values using the integrated Arrhenius equation.

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TABLE I

EXPERIMENTAL VALUES OF VELOCITY CONSTANTS AS A FUNCTION OF DIELECTRIC CONSTANT; CORRESPONDING ENERGIES OF ACTIVATION AND FREQUENCY FACTORS

Temperature 25.13° C

Ionic Strength = 0.0200 HCl = 0.0200M Ester = 0.0100M

% by Wt. Acetone	D	$k' \times 10^4 \text{min}^{-1}$	$\frac{k'}{C_{H_2O}} \times 10^6 \text{min}^{-1}\text{mol}^{-1}$	$\triangle E \times 10^{-3}$ (25.13° C-35.21° C)	B (25.13° C-35.21° C)
0.00	78.49	1.42	2.57	16.6	15.1
8.04	74.54	1.31	2.63	16.0	15.1
16.43	69.50	1.20_9	2.73	16.7	15.4
25.21	64.00	1.05_4	2.72	16.7	15.4
34.40	58.53	0.92_1	2.77	16.8	15.5
44.03	52.00	0.79_5	2.87	16.8	15.6
64.73	38.90	0.54_1	3.26	16.7	15.6
75.88	32.04	0.44_9	4.06	18.2	18.2

Temperature 35.21° C

				$\triangle E \times 10^{-3}$ (35.21° C-45.48° C)	(35.21° C-45.48° C)
0.00	74.85	3.54	6.41	16.2	14.5
8.63	70.63	3.16	6.37	15.2	12.8
16.26	65.92	3.02_8	6.86	15.8	13.9
24.97	60.81	2.64_8	6.85	14.4	11.6
34.11	55.46	2.31_5	6.99	15.9	14.0
43.71	49.90	2.00_4	7.26	15.3	13.2
53.81	43.35	1.65_8	7.51	16.4	15.0
64.44	37.15	1.35_9	8.21	18.3	18.1
75.65	30.55	1.22_1	11.06	18.6	18.9

Temperature 45.48° C

% by Wt. Acetone	D	$k' + 10^4 \text{min}^{-1}$	$\frac{k'}{C_{H_2O}} \times 10^6 \text{min}^{-1}\text{mcl}^{-1}$
3.89	69.66	7.25_4	13.90
7.87	67.61	7.00_1	14.16
24.77	55.46	5.61_9	14.61
33.87	53.21	5.30_8	16.10
43.45	47.53	4.46_8	16.27
53.54	41.70	3.91_5	17.81
64.19	35.28	3.53_5	21.45
75.45	29.24	3.22_4	29.34

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The numerical values of these quantities are those observed in many instances for reactions in solution.

In Fig. 1 is plotted log k'/C_{H_2O} versus $1/D$ for the three temperatures at which data were taken. These plots are straight lines in the regions of higher dielectric constant and the slopes are of the sign and magnitude expected for reactions between ions of positive sign and dipolar molecules. Using the equation

$$\log k'_D = \log k'_{D=\infty} + \frac{Z\,\varepsilon\,\mu}{2.303\ DkTr^2} \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

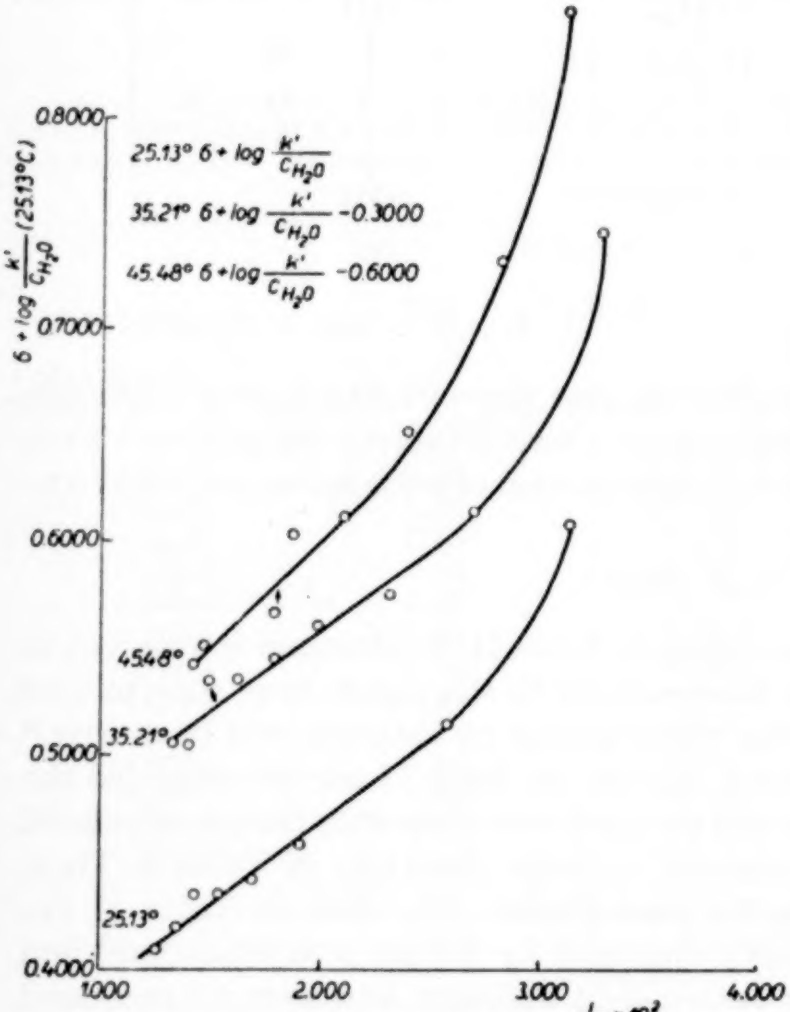


Fig. 1

where k'_D is the specific velocity constant at a given dielectric constant D.

$k'_{D=\infty}$ is the specific velocity constant at reference dielectric constant of infinity.

μ is the dipole moment of the molecule

r = distance of approach for reaction between ion and molecule

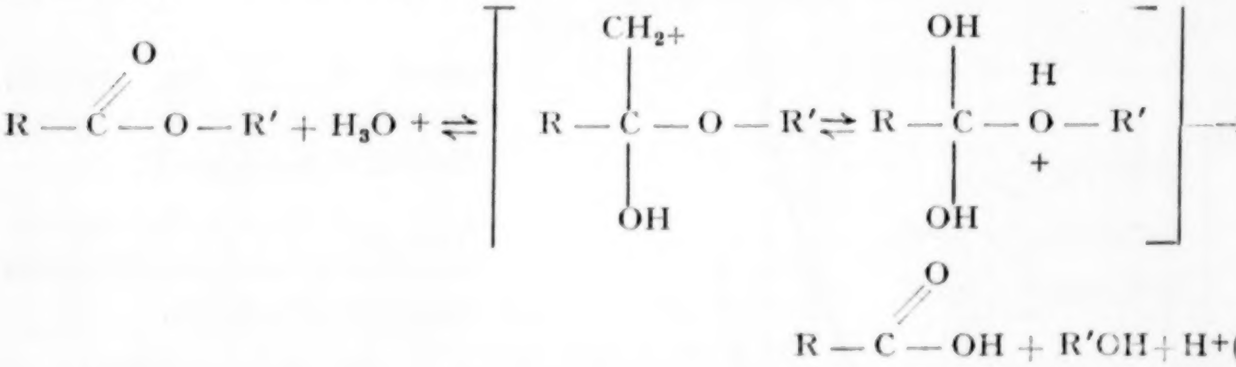
k = Boltzmann constant

the slopes of the lines in Fig. 1 can be used to calculate the quantity r. If data and theory are in agreement the values of r found should be a molecular dimension since it is essentially the radius of the intermediate in the kinetic process. The calculation would be

$$\text{Slope} = S = \frac{Z\,\varepsilon\,\mu}{2.303\ kTr^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$\text{or} \quad r = \sqrt{\frac{Z\,\varepsilon\,\mu}{2.303\ SkT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

The value of the moment for methyl propionate was not found in the literature but was taken to be 1.8 Debye units to agree with the moments of methyl and ethyl acetate and ethyl propionate which were recorded[8] as 1.7, 1.8, 1.79 Debye units respectively. Using this value of the moment r was found from equation (4) to be 3.43, 3.42, and 3.01 A at 25.13, 35.21, and 45.48° C respectively. We feel that these values are consistent with ion-dipole theory with respect to the acid hydrolysis of this ester. The signs of the slopes in Fig. 1 not only confirm the predictions of equation (2), above, but are also in agreement with the theory of GLASSTONE, LAIDLER AND EYRING[9] with respect to reactions between ions and neutral molecules. . . . .



$$R-\overset{\overset{O}{/\!/}}{C}-O-R' + H_3O^+ \rightleftharpoons \left[R-\underset{OH}{\overset{CH_{2+}}{C}}-O-R' \rightleftharpoons R-\underset{OH}{\overset{OH}{C}}-\underset{+}{\overset{H}{O}}-R' \right] \rightarrow R-\overset{\overset{O}{/\!/}}{C}-OH + R'OH + H^+ \quad (5)$$

With respect to the ion-dipole mechanism, that given by BENDER[11] is applicable to an ion-dipole reaction if the first step or a step involving the product of the concentration of a positive ion and the concentration of a dipolar molecule governs the rate.

SALT EFFECT

Values of k' as a function of μ are given in Table II. A minimum is observed in the velocity constant at all three temperatures in the region from 0.05 to 0.08 ionic strength. A similar phenomenon was observed by HARNED AND PFANSTIEL[11] in the case of acid hydrolysis of ethyl acetate. In Table II are also recorded the values of the energies of activation and the Arrhenius frequency factors calculated by the methods described with reference to these quantities in Table I. These values are of expected magnitude for rate studies. The data in Table II are reminiscent of the catalytic catenary discussed by EULER AND OLANDER[12] and more recent authors[13,14]. Since the activities of hydrogen ions were not measured during the time of the runs these activities were obtained by calculating the activity coefficients of the ions using the Debye-Hückel first approximation.

The equation for this first approximation is

$$-\ln f_{H_3O^+} = \frac{Z^2_{H_3O^+} A\sqrt{\mu}}{1 + B a_i \sqrt{\mu}} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where $f_{H_3O^+}$ is the activity coefficient of the hydronium ion of valence $Z_{H_3O^+}$ in a solution of ionic strength μ; A and B are the Debye-Hückel constants, which can be calculated from the known properties of the solvent and certain physical constants, and a_i is the distance of closest approach of two ions. The values of a_i used at the different temperatures were the values of r found from the plots of log (k'/C_{H_2O}) versus $1/D$. The concentration of the hydronium ion used in the calculation of the activity of the ion was assumed to be the same as the concentration of the acid. Logarithms of the specific velocity constants were plotted against the negative logarithms of the activity of the hydronium ion (*i.e.* pH). The curves shown in Fig. 2 were obtained. These curves have the expected shape of the catalytic catenary postulated by the theory of EULER[13]. This theory is still applicable to particular reactions. The curves described belong to type "b" catenary discussed by BELL[14], *i.e.* the sides of the catenary intersect at a sharp

TABLE II

EXPERIMENTAL VALUES OF VELOCITY CONSTANTS AS A FUNCTION OF IONIC STRENGTH; CORRESPONDING ENERGIES OF ACTIVATION, FREQUENCY FACTORS, AND ACTIVITY COEFFICIENTS

Temperature 25.13° C

$D = 78.49$ HCl $= 0.0200 M$ Ester $= 0.0100 M$

Total Ionic Strength	$k' \times 10^4 \text{min}^{-1}$	$f_{H_3O^+}$	$\Delta E \times 10^{-3}$ (25.13° C - 35.21° C)	B (25.13° C - 35.21° C)
0.0200	1.42	0.867	16.6	19.1
0.0300	1.41	0.844	16.5	19.0
0.0400	1.40^4	0.826	16.6	19.2
0.0600	1.38	0.799	16.6	19.3
0.0800	1.38^7	0.778	16.8	19.3
0.1000	1.38	0.761	17.0	19.2
0.1200	1.39^2	0.747	17.2	20.2
0.1700	1.41	0.719	17.2	20.2
0.2200	1.42	0.698	17.2	20.2
0.2700	1.42	0.681	17.2	20.1
0.3200	1.43^8	0.667		
0.4200	1.44^4	0.645		
0.5200	1.45^4	0.631		

Temperature 35.21

			$E \times 10^{-3}$ (35.21° C - 45.48° C)	B (35.21° C - 45.48° C)
0.0200	3.54	0.864	16.1	18.3
0.0300	3.52	0.841	16.1	18.3
0.0400	3.50	0.823	16.0	18.2
0.0500	3.49^5	0.808	16.1	18.2
0.0600	3.47	0.795	16.1	18.3
0.0700	3.46	0.784	16.1	18.2
0.0800	3.48	0.774	15.0	18.0
0.0900	3.49	0.765	15.8	17.9
0.1000	3.53^5	0.757	15.6	17.6
0.1400	3.59^5	0.730	15.7	17.7
0.1800	3.64	0.710	16.0	18.2
0.2200	3.67	0.693	16.1	18.3
0.2600	3.68	0.679	16.1	18.4

TABLE II
(Continued)

Temperature 45.48° C		
Total Ionic Strength, μ	$k' \times 10^4$ min^{-1}	$f_{H_3O^+}$
0.0200	8.25	0.860
0.0300	8.20	0.835
0.0400	8.15	0.816
0.0500	8.11	0.800
0.0600	8.08	0.787
0.0700	8.05	0.775
0.0800	8.04	0.764
0.0900	8.03	0.755
0.1000	8.05	0.746
0.1200	8.13	0.731
0.1400	8.20	0.718
0.1600	8.38	0.706
0.1800	8.45	0.695
0.2200	8.55	0.678
0.2600	8.58	0.670

minimum and slope upward at angles of approximately forty-five degrees with the horizontal. The elevation of the intersection point of the two branches of the curve above the zero value of the ordinate indicates a marked water catalyzed reaction. OLANDER[15] has observed this minimum in the saponification of esters and sulfonic acid esters.

The neutral salt effect observed here is not that which would be found in the case of a weak-acid catalyst in the presence of its salt, but the salt effect in this case is exerted through the ionic strength effect on the hydronium ion coming from a completely dissociated strong acid. The classical theory of EULER has been modified by addi-

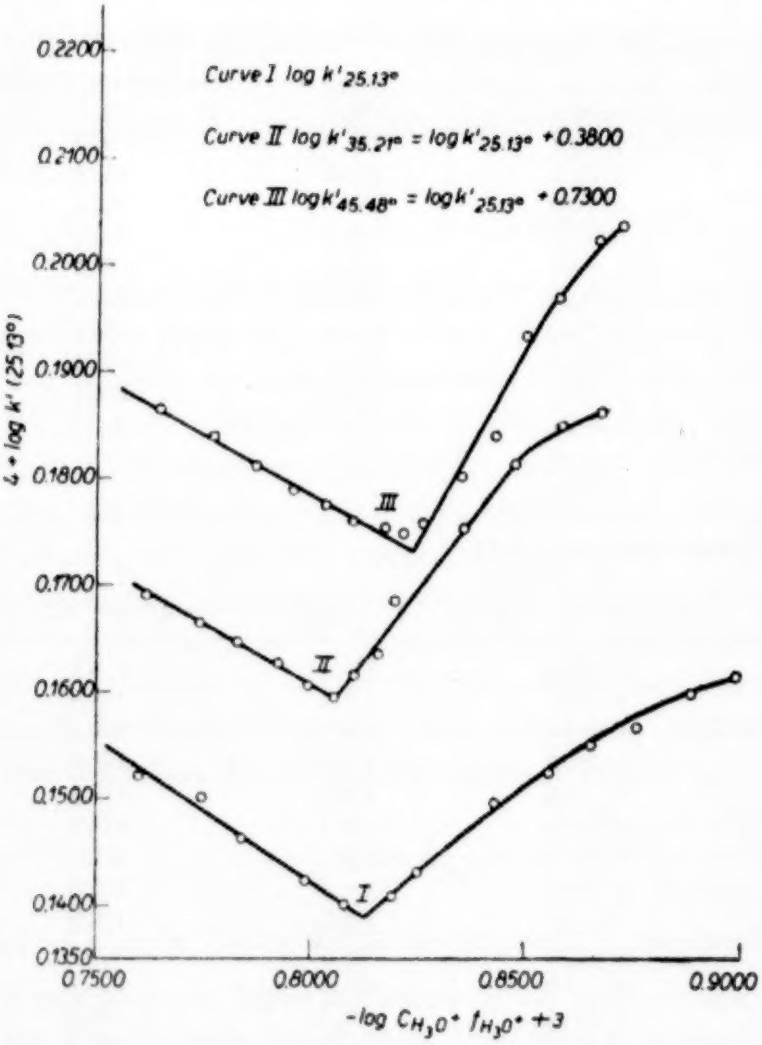


Fig. 2

tional assumptions so as to be in harmony with modern theory of acid-base catalysis.

The occurrence of a measurable "water reaction", together with catalysis by hydrogen or hydroxyl ions, is sufficient to characterize a reaction as being catalyzed by acids or bases in general. Since there is a water reaction in the hydrolysis of esters in aqueous medium, and since there is a catalysis of the hydrolysis by hydronium ion, these reactions are subject to general acid-base catalysis.

ACKNOWLEDGEMENT

We wish to acknowledge the many helpful discussions on certain aspects of this problem with Drs ARTHUR FRY and SAMUEL SIEGEL.

SUMMARY

The hydrolysis of methyl propionate catalyzed by hydrochloric acid has been studied at three temperatures in water-acetone media and in water media containing different concentrations of sodium nitrate. The specific velocity constants in water-acetone media were shown to conform to the theory for reaction between positive ions and dipolar molecules. BENDER's mechanism for ester hydrolysis has been accepted as plausible in view of the kinetics in mixed media. The specific velocity constants in the sodium nitrate solutions were shown to conform to the theory of EULER.

RÉSUMÉ

L'hydrolyse du propionate de méthyle, catalysée par l'acide chlorhydrique, a été étudiée à 3 températures différentes, dans les milieux: eau-acétone et eau, renfermant différentes concentrations de nitrate de sodium. Les constantes de vitesse spécifique dans le milieu eau-acétone correspondent à la théorie des réactions entre ions positifs et molécules dipolaires. Le mécanisme de BENDER sur l'hydrolyse des esters peut être considéré comme plausible. Les constantes de vitesse spécifique dans les solutions de nitrate de sodium concordent bien avec la théorie d'EULER.

ZUSAMMENFASSUNG

Die von Salzsäure katalysierte Hydrolyse von Propionsäuremethylester wurde in Wasser-Aceton und in verschiedene Konzentrationen von Natriumnitrat enthaltendem, wässrigem Medium bei drei Temperaturen untersucht. Es wurde gezeigt, dass die spezifischen Geschwindigkeitskonstanten in Wasser-Aceton-Medium übereinstimmten mit der Theorie für die Reaktion zwischen positiven Ionen und dipolaren Molekülen. BENDER's Mechanismus für die Esterhydrolyse wurde als plausibel in Hinblick auf die Kinetik in gemischten Medien angenommen. Es wurde gezeigt, dass die spezifischen Geschwindigkeitskonstanten in den Natriumnitratlösungen mit der Theorie von EULER übereinstimmen.

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THE DIELECTRIC CONSTANT EFFECT UPON THE ACID HYDROLYSIS OF ETHYL ACETATE*

by

P. MADHAVAN NAIR AND EDWARD S. AMIS

Chemistry Department, University of Arkansas, Fayetteville, Arkansas (U.S.A.)

It was thought of interest to study the dielectric constant effect upon the rate of acid hydrolysis of ethyl acetate from the standpoint of electrostatics and compare these resulte with those of the acid hydrolysis of methyl propionate. The latter reaction was studied by HOCKERSMITH AND AMIS[1] at three temperatures in acetone-water solvents of different percentages by weight of acetone and therefore different dielectric constants. These authors found that the specific velocity constants conform to the theory for reaction between positive ions and dipolar molecules as expressed by the equation[2]

$$\log k_D' = \log k'_{D=\infty} + \frac{Z \varepsilon \mu}{2.303\ DkTr^2} \quad \dots\dots\dots\dots\dots \quad (1)$$

In this equation k_D' is the specific velocity constant at a given dielectric constant D, $k'_{D=\infty}$ is the specific velocity constant at a reference dielectric constant of infinity, μ is the dipole moment of the molecule, Z is the valence of the ion, ε is the electronic charge, r is the distance of approach for reaction between the ion and molecule (the radius of the intermediate complex), k is the Boltzmann gas constant, and T the absolute temperature.

From this equation a plot of log k' versus $1/D$ should yield a straight line. The slope of this line should be positive for a positive ionic reactant and negative for a negative ionic reactant. The magnitude of the slope should be equal to $\frac{Z \varepsilon \mu}{2.303\ kTr^2}$, and from it a molecular dimension should be obtainable for r. HOCKERSMITH AND AMIS[1] found values or r of 3.43 A, 3.42 A, and 3.01 A at 25.13° C, 35.21° C, and 45.48° C, respectively, for the hydrolysis of methyl propionate by hydrochloric acid in water-acetone solvents.

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* This work was done on a contract made by the Institute of Science and Technology of the University of Arkansas with the Office of Naval Research.

References p. 115.

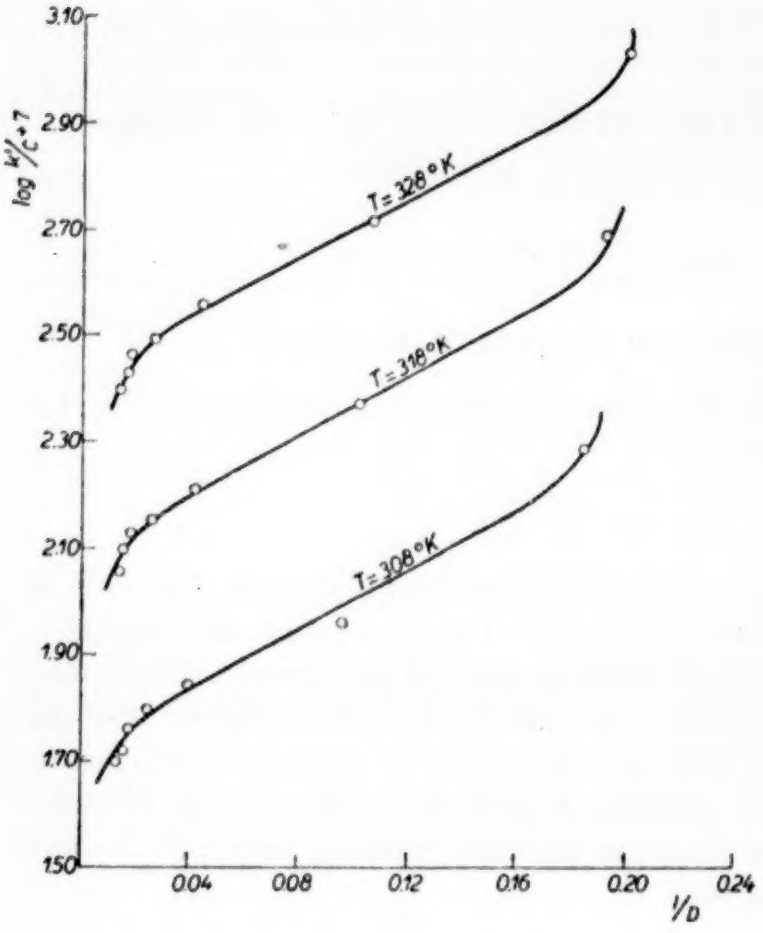

Fig. 1. Dioxan-water.

Nair and Anantakrishnan[3] have studied the hydrolysis of ethyl acetate by hydrochloric acid in dioxane-water and in acetone-water solvents of 0 to 90% compositions of the organic components of the solvents. They made a qualitative treatment only of their data from the standpoint of electrostatics, and hence in order to compare these data with those on methyl propionate the electrostatic approach is presented in what follows.

In Fig. 1 are plotted the logarithms of the quotients of the values of the specific velocity constant k' divided by the concentrations of water, C, in the samples, versus the reciprocals of the dielectric constants D for the dioxane-water solvents. The downward curvature of the plots at low values of $1/D$ (high values of D) are reminiscent of the curvature downward of a similar plot of the data of Svirbely and Schramm[4,5] for the ion-ion reaction between ammonium ion and cyanate ion in water-methyl alcohol solvents. The departure from linearity of the curves at high values of $1/D$ (low values of D) has frequently been mentioned[6,7] in the case of ion-ion reactions.

Taking the slope of the long, straight central portions of the curves in Fig. 1 and calculating the values of r as explained above, one obtains 9.08 A, 9.18 A, and 9.50 A, for the values of r at 35°, 45°, and 55° C, respectively, from the data for the acid hydrolysis of ethyl acetate in dioxane-water solvents. These are reasonable values of the parameter, r.

Expanded $\log \dfrac{k'}{C}$ versus $1/D$ plots for the same data for the low values of $1/D$ (high values of D) are themselves linear except for the very lowest regions of $1/D$. The slopes, however, are steeper than the extensive central regions of the plots in Fig. 1. Therefore the limiting values of r calculated from this limited range of $1/D$ would be smaller than these calculated from the plots in Fig. 1, and are 7.0 A, 7.5 A, and 7.3 A, respectively, at 35°, 45 °, and 55° C.

References p. 115.

Plots of log $\frac{k'}{C}$ versus $1/D$ of Nair and Anantakrishnan's[3] data for the acid hydrolysis of ethyl acetate in acetone-water solvents are given in Fig. 2. In these plots the curvature downward in the regions of low $1/D$ values is not noticeable. However, the slopes of the straight portions of the plots decrease with increasing temperature and the curve at 55° has an almost horizontal straight portion. The values of r therefore increase with increasing temperature and are 5.21 A and 6.19 A at 35° and 45° C, respectively. The value of r at 55° C was not calculated since the small slope of the straight line portion of the curve at this temperature would yield an unreasonably large value of r.

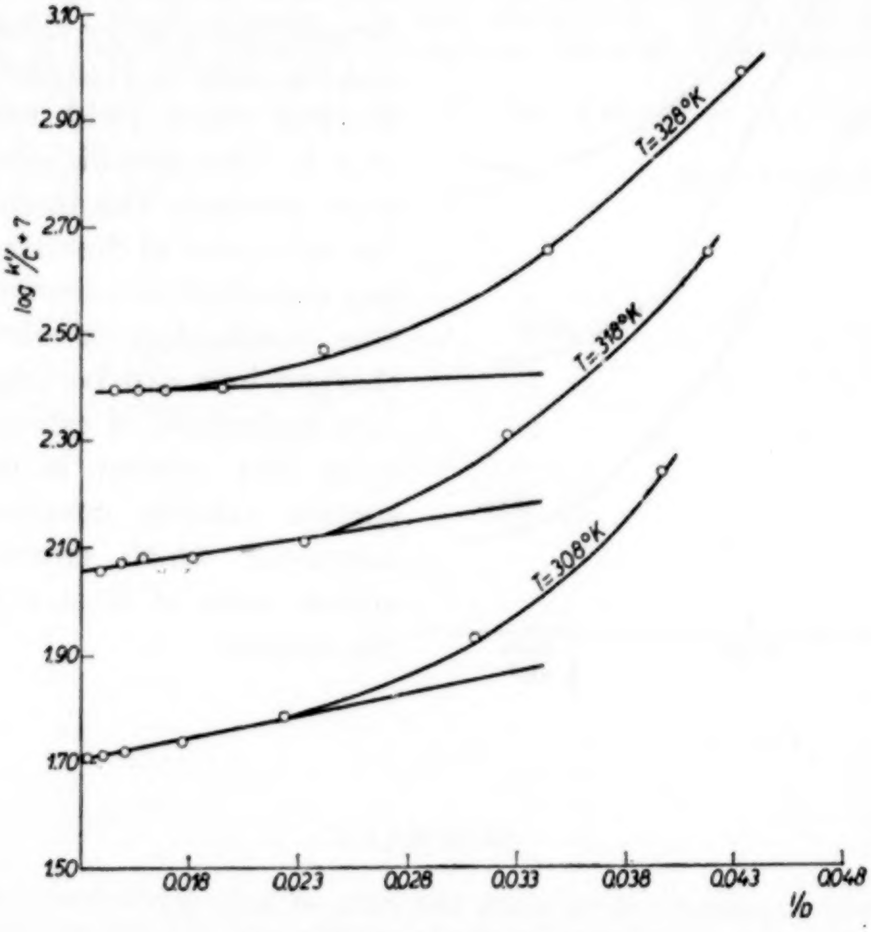

Fig. 2. Acetone-water.

Evidently a specific solvent effect is becoming more pronounced the higher the temperature, and at 55° C practically masks the electrostatic influence of the dielectric constant.

It might be pointed out that plots of log k' versus $1/D$, where the values of k' have not been divided by the concentrations of water, yield straight lines of negative slope. The sign and magnitude of these slopes are those required by reactions between ions of like sign. In Fig. 3 the data of Hockersmith and Amis[1] are plotted in this manner: The slopes using the Brønsted-Christiansen-

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Scatchard equation for ionic reactants yield r values of 6.44 A, 6.88 A, and 6.26 A at 25.13° C, 35.21° C, and 45.48° C, respectively. The plots of NAIR AND ANANTAKRISHNAN's data yield similar curves as do the data of HARNED AND ROSS[8] for the acid hydrolysis of methyl acetate in dioxane-water solvents. The data of NAIR AND ANANTAKRISHNAN in acetone-water media give r values of about 5.5A; however, the data of these authors in dioxane-water give r values about 27.4 A and the data of HARNED AND ROSS in dioxane-water yield values of about 18.7 A. Thus specific solvent effects are quite evident. The main objections to the treatment of the data in the manner just described are: first, that no reasonable mechanism involving two like charged ions can be originated for the acid hydrolysis of esters; and second, it is not correct in calculating the specific velocity constant to ignore a substance which enters into the reaction even if it is a component of the solvent.

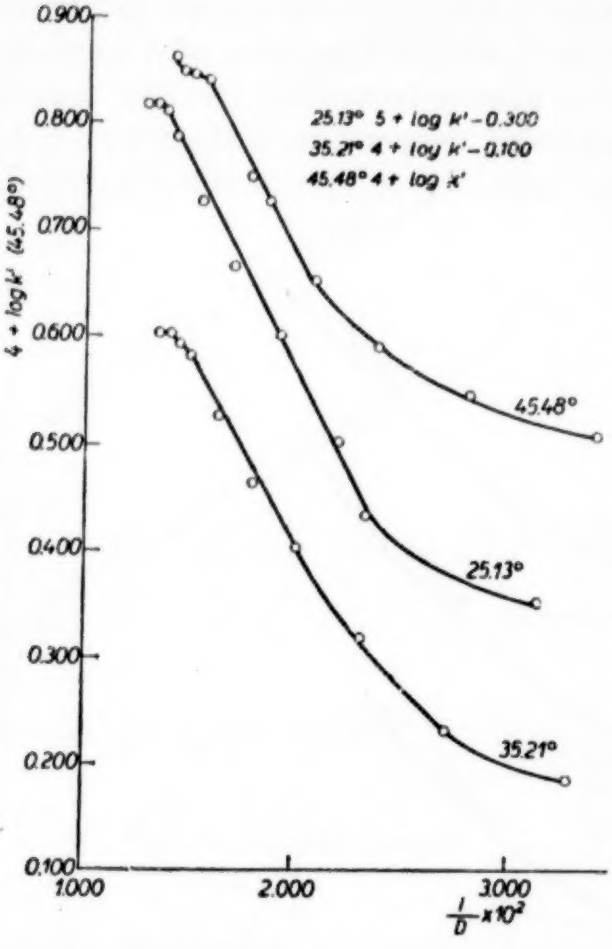

Fig. 3.

SUMMARY

The dielectric constant effect upon the rate of acid hydrolysis of ethyl acetate is presented from the standpoint of electrostatics and the results compared to like effects upon the acid hydrolysis of methyl propionate.

RÉSUMÉ

L'effet de la constante diélectrique sur l'hydrolyse acide de l'acétate d'éthyle est envisagé du point de vue électrostatique et les résultats sont comparés à ceux de l'hydrolyse acide du propionate de méthyle.

ZUSAMMENFASSUNG

Der Effekt der Dielektrizitätskonstante auf die Hydrolysengeschwindigkeit von Äthylacetat mit Säure wird vom elektrostatischen Standpunkt dargelegt und die Ergebnisse mit ähnlichen Effekten bei der Säurehydrolyse von Propionsäuremethylester verglichen.

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THE APPLICATION OF THIOSALTS IN ANALYSIS
I. COMPLETE PRECIPITATION OF SULPHIDES

by

I. K. TAIMNI AND R. P. AGARWAL

Chemical Laboratories, University of Allahabad, Allahabad (India)

The different schemes of qualitative analysis used at present for the common as well as the so-called "rare" elements are merely modifications of the scheme devised by NOYES, BRAY AND SPEAR[1] long ago. This scheme follows, in the main outline, the classical scheme of FRESENIUS in which the precipitation of sulphides acid and alkaline solutions is used for the separation of whole groups of metallic ions from one another.

One of the chief defects of this scheme is the great difficulty experienced in precipitating completely all the metals of the copper and arsenic groups from a hydrochloric acid solution. While the precipitation of mercury, lead, bismuth, copper, cadmium, antimony, tin, gold, selenium and tellurium does not involve any special difficulty, that of the three metals, arsenic (when it is present in the form of arsenate), molybdenum and platinum is extremely slow and generally incomplete, and consequently it becomes difficult to adopt the scheme in a class containing a large number of students. Selenium also, though it is precipitated fairly rapidly gives a good deal of trouble. When a solution containing selenium is treated with hydrogen sulphide in a hot acid solution the metal is frequently precipitated as a vitreous mass which resists the solvent action of not only yellow ammonium sulphide, but also of the strongest oxidizing solvents like concentrated nitric acid, aqua regia or a mixture of concentrated nitric acid and potassium chlorate. The only common reagent which can dissolve this form of selenium is hot, concentrated caustic potash or caustic soda.

The precipitation of molybdenum, platinum and arsenic is usually carried out with the help of a pressure bottle. This facilitates considerably the precipitation of the metals, but it has been found that, in spite of subjecting the mixture to this elaborate procedure for half an hour, the metals are still not completely precipitated. The unsatisfactory nature of the usual method adopted for the precipitation of these metals as sulphides will be seen from the following remarks by HILLEBRAND[2] about the precipitation of molybdenum sulphide. "Although the sulphide of molybdenum is insoluble in non-oxidizing acids, its complete precipitation is a difficult matter, particularly in hydrochloric acid solution or in the presence of impurities such as vanadium. Incomplete precipitation is caused by a reduction of part of the molybdate by hydrogen sulphide. The reduced compound is then very slowly precipitated even in a pressure bottle, and the only safe procedure lies in filtering, washing the precipitate, boiling the filtrate to expel hydrogen sulphide, oxidizing the reduced molybdenum, as for example, with persulphate and again precipitating with hydrogen sulphide".

In view of these difficulties encountered in precipitating the metals of the copper and arsenic groups as sulphides in acid solutions the authors undertook a thorough investigation of the conditions under which the sulphides of the three metals, molybdenum, platinum and arsenic, can be precipitated quickly and completely without the use of the pressure bottle. As a result of these investigations[3] it was found that the formation of thiosalts and their subsequent decomposition with excess of hydrochloric acid provides the quickest method of precipitating these metals completely as sulphides. The solution containing the metals is treated with excess of concentrated ammonia, hydrogen sulphide is passed into the solution, the thiosalts thus formed decomposed by adding excess of hydrochloric acid, when the sulphides of these three metals are precipitated immediately along with the sulphides of all the other metals of the copper-arsenic group. The precipitation of these metals can be brought about not only without any considerable loss of time but is so thorough that not even a trace of the elements can be detected in the filtrate by the usual methods.

The following table gives some idea of the comparative efficiency of the two methods in the precipitation of sulphides when solutions containing the three metals were treated with hydrogen sulphide in acid and alkaline solutions.

Further investigation showed that it was not at all necessary to pass hydrogen sulphide into the solution after adding a large excess of concentrated ammonia. A concentrated solution of ammonium sulphide, prepared by passing hydrogen sulphide in liquor ammonia, can be kept as a shelf reagent and is equally effective in forming the thiosalt immediately. All that is necessary to precipitate the sulphides of the metals is to treat the solution with the required excess of this reagent and then to add excess of hydrochloric acid for decomposing the thiosalt.

TABLE I

Metal	Amount of metal remaining in filtrate after precipitation in acid solution (for about 1 hour)	Amount of metal remaining in filtrate after precipitation of sulphide from thiosalt
Molybdenum	Appr. 5%	No trace
Platinum	Appr. 1%	No trace
Arsenic (as arsenate)	Appr. 2%	No trace

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This brings about a further saving of time and eliminates the use of hydrogen sulphide gas.

At first it may seem remarkable that metals like molybdenum, platinum and arsenic can be completely converted into their thiosalts by merely adding a sufficient excess of concentrated ammonium sulphide solution but the results obtained show conclusively that such is the case, and this fact may be utilised in precipitating quickly and completely the sulphides of these metals. The saving of time effected in this manner is considerable. While it is not possible, for example, to ensure the complete precipitation of arsenic in arsenate even in an hour by passing hydrogen sulphide in an acid solution, this can be accomplished easily in a few minutes by adopting the method given above.

Behaviour of other metals of arsenic group

The other metals of the arsenic group which form thiosalts with yellow ammonium sulphide are gold, selenium, tellurium, antimony and tin. Solutions containing these metals were treated with concentrated ammonium sulphide solution in the same manner as solutions of molybdenum, platinum and arsenic. In every case they were changed into the corresponding thiosalt immediately and on adding an excess of $2N$ hydrochloric acid the metal was completely precipitated as sulphide and not even a trace of the metal was found in the filtrate. It was found, however, that tin must be in the stannic form to form thiosalt even with concentrated ammonium sulphide solution.

Behaviour of vanadium

Vanadium is not precipitated as sulphide on passing hydrogen sulphide in acid solution. But as it forms a thiosalt which on acidification gives a precipitate of sulphide, we investigated particularly the behaviour of vanadium salts with concentrated ammonium sulphide solution. On adding concentrated ammonium sulphide solution in large excess to a solution containing a vanadate, a coloured solution is formed in which most of the vanadium is presumably present as a thiosalt. On acidifying this solution with hydrochloric acid, boiling, and filtering off the precipitate which is formed, the filtrate is found to have a blue colour showing that vanadium has only been partly precipitated. In the case of molybdenum the incomplete precipitation of the metal by hydrogen sulphide from an acid solution is supposed to be due to the partial reduction of the molybdate to a lower state of oxidation. Working on the assumption that a similar cause may be operating in the incomplete precipitation of vanadium also, we tried the action of various oxidizing agents on the vanadate solution before treating it with ammonium sulphide solution. Previous oxidation with oxidizing agents like concentrated nitric acid, fuming nitric acid, a mixture of concentrated nitric

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acid and potassium chlorate, and aqua regia failed to bring about complete precipitation of vanadium as sulphide. In every case the filtrate showed the slight blue colour of quadrivalent vanadium. But when an acidified solution of vanadate was treated with hydrogen peroxide before treatment with concentrated ammonium sulphide solution the precipitation of vanadium was found to be quite complete and not a trace of the metal could be detected in the filtrate. The ammonium sulphide reagent must, however, be added to the solution containing a slight excess of hydrogen peroxide even though this gives a precipitate of sulphur. If the solution is boiled to decompose excess of hydrogen peroxide before adding ammonium sulphide, the precipitation of vanadium is incomplete as in previous cases.

SUMMARY

1. A new method of precipitating completely and quickly molybdenum, platinum and arsenic (in arsenates) as sulphides has been described.

2. The new method is based upon the immediate formation of thiosalts of these metals by adding concentrated ammonium sulphide and the subsequent decomposition of the thiosalt by adding excess of hydrochloric acid.

3. The great usefulness of the method in qualitative analysis lies not only in the completeness of precipitation of the metals but also in the remarkable saving in the time taken to precipitate the metals.

4. It has been shown that the method is applicable also to all the other metals of the arsenic group.

5. Selenium which is precipitated by decomposing the thiosalt is easily soluble in ammonium sulphide while the selenium precipitate from a hot acid solution is generally in a form ~~which is~~ insoluble.

6. Vanadium can be precipitated completely with the arsenic group by this method if it is previously treated with hydrogen peroxide.

7. The use of the hydrogen sulphide gas has been replaced by a far more convenient reagent-concentrated ammonium sulphide.

RÉSUMÉ

1. Une nouvelle méthode de précipitation quantitative et rapide est décrite pour le dosage du molybdène, du platine et de l'arsenic (à l'état d'arséniates) comme sulfures.

2. Cette nouvelle méthode est basée sur la formation immédiate de thiosels de ces métaux par addition de sulfure d'ammonium concentré et sur la décomposition du thiosel formé par addition d'acide chlorhydrique en excès.

3. La grande utilité de cette méthode d'analyse qualitative repose non seulement sur la précipitation quantitative mais aussi sur le remarquable gain de temps pour précipiter les métaux.

4. La méthode est appliquable aussi à tous les autres métaux du groupe de l'arsenic.

5. Le sélénium précipité par décomposition du thiosel est facilement soluble dans le sulfure d'ammonium tandis que les sélénium précipité à chaud, en solution acide est généralement sous une forme insoluble.

6. Le vanadium peut être précipité quantitativement avec les éléments du groupe de l'arsenic, si on le traite au préalable par le peroxyde d'hydrogène.

7. L'hydrogène sulfuré a été remplacé par le sulfure d'ammonium en solution concentrée (d'un emploi plus pratique).

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ZUSAMMENFASSUNG

1. Eine neue Methode der vollständigen und raschen Ausfällung von Molybdän, Platin und Arsenat (in Arsenaten) als Sulfide wurde beschrieben.

2. Die neue Methode gründet sich auf die sofortige Bildung von Thiosalzen dieser Metalle beim Hinzufügen von konz. Ammoniumsulfid und die darauffolgende Zersetzung der Thiosalze beim Hinzufügen eines Überschusses von Salzsäure.

3. Der grosse Vorteil dieser Methode bei der qualitativen Analyse liegt nicht nur in der Vollständigkeit der Ausfällung der Metalle, sondern auch in der beträchtlichen Zeitersparnis bei der Ausfällung der Metalle.

4. Es wurde gezeigt, dass sich die Methode auch auf alle anderen Metalle der Arsengruppe anwenden lässt.

5. Durch Zersetzung des Thiosalzes ausgefälltes Selen ist leicht löslich in Ammoniumsulfid, während das aus heisser Säurelösung ausgefällte Selen im allgemeinen in unlöslicher Form vorliegt.

6. Mit dieser Methode kann Vanadium mit der Arsengruppe vollständig ausgefällt werden, wenn es zuerst mit Wasserstoffperoxyd behandelt wird.

7. Der Gebrauch von Schwefelwasserstoffgas wurde durch das weit bequemere konz. Ammoniumsulfidreagenz ersetzt.

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THE APPLICATION OF THIOSALTS IN ANALYSIS
II. ESTIMATIONS BASED ON DECOMPOSITION OF THIOSALTS
Part A. ESTIMATION OF ARSENIC, SELENIUM AND TELLURIUM

by

I. K. TAIMNI AND R. P. AGARWAL

Chemical Laboratories, University of Allahabad, Allahabad (India)

In a previous paper[1] it was shown by the authors that the precipitation of the copper-arsenic groups by first adding concentrated ammonium sulphide and then acidifying the mixture solves not only the problem of quick and complete precipitation of molybdenum, platinum and arsenic but also that of obtaining selenium in the form of a precipitate which is easily soluble in ammonium sulphide. The ease with which the complete precipitation of these elements can be brought about by first forming and then decomposing the thiosalts showed the possibility of the method being used for the gravimetric estimation of elements which form thiosalts. The present investigation was undertaken with a view to ascertain how far the precipitation of sulphides from thiosalts could be utilized for the gravimetric estimation of such elements. A quantitative study of this nature was also considered essential if the easy formation of thiosalts and their complete decomposition is to be utilized in simplifying the scheme of qualitative analysis for the basic radicals.

In a preliminary quantitative study of the decomposition of thiosalts it was found that the elements which are capable of forming thiosalts can be divided into three characteristic groups. In the first group we may place elements like arsenic, selenium and tellurium. On decomposing the thiosalts of these elements a pure precipitate of the sulphide, corresponding with the formulas As_2S_5, SeS_2, and TeS_2, is obtained and this can be weighed as such for the gravimetric estimation of the elements. In the second group may be placed elements like molybdenum and tin which also give a precipitate of the sulphide on decomposing the thiosalt but the weight of the precipitate does not correspond with the usual formulas of the sulphides MoS_3 and SnS_2. However, the weight of the precipitate is directly proportional to the quantity of the element precipitated as sulphide, and therefore, it is possible to estimate it by multiplying the weight of the precipitate by a known factor. In the third group may be placed elements like gold, platinum and vanadium which cannot be estimated gravimetrically by weighing the precipitate obtained on decomposing the thiosalts. Although the thiosalt is decomposed

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immediately and the element is precipitated completely as sulphide, the precipitate on weighing does not give a constant weight.

Materials. The most important of these is the alkali sulphide solution which is required for forming the thiosalts of the elements. This is prepared either from ammonium hydroxide or 2*N* sodium hydroxide. In each case the alkali solution is saturated with hydrogen sulphide from a Kipp's apparatus, the gas being previously purified by passing it through water contained in two wash bottles. The temperature of the alkali sulphide solution should not be allowed to rise above 20° C as oxidation takes place quickly at higher temperatures resulting in the appearance of a slightly yellow colour in the solution. This will give a precipitate of sulphur when the solution is acidified with hydrochloric acid after the formation of thiosalts. The formation of free sulphur must be avoided in estimations where the precipitate cannot be washed with carbon bisulphide, as for example, in the case of selenium and tellurium. The solution of ammonium sulphide or sodium sulphide must be freshly prepared, preferably at a temperature below 10° C and must be tested with hydrochloric acid before being used in any estimation, otherwise results are liable to be too high.

The other materials used in the various estimations were of B.D.H. AnalaR quality or Kahlbaum's. The solutions prepared from these materials were carefully standardized by well-known methods.

EXPERIMENTAL

Estimation of arsenic as As_2S_5 in solution of arsenates

Arsenic in the pentavalent state can be estimated gravimetrically either by precipitation[2] as As_2S_5 from an ice-cold solution containing concentrated hydrochloric acid or as $MgNH_4AsO_4$ with magnesia mixture[3]. Both the methods take inordinately long time and are tedious. In the former, it is necessary to pass hydrogen sulphide into the arsenate solution for at least an hour, and for complete precipitation to let it stand for another hour. In the latter method the arsenate solution has to be kept overnight after adding the magnesia mixture. As compared with both these methods the precipitation of As_2S_5 by decomposing the thiosalt is remarkably simple and the whole estimation can be completed in about an hour as the following procedure will show.

Solutions of potassium arsenate were prepared from a pure sample of the salt and the arsenic content in each determined volumetrically by precipitating[4] the arsenate in solution as silver arsenate and estimating the silver in the precipitate by VOLHARD's method. Measured volumes of the arsenate solutions were then treated with a large excess of the alkali sulphide solution, about 10 ml of the alkali sulphide solution being required for every 50 mg of arsenic. The solution was then treated with sufficient concentrated hydrochloric acid to neutralize the alkali and produce a concentration of approximately 6*N* hydrochloric acid in the resulting mixture. The mixture was heated to boiling, stirred thoroughly and allowed to stand for about 10 minutes. The precipitate of arsenic sulphide was then filtered through a weighed Gooch or sintered glass crucible (porosity 4), washed thoroughly with distilled water, alcohol and ether successively, sucked dry at the filter pump for about 5 minutes, dried in a vacuum desiccator and weighed after 30 minutes. Alternatively, the precipitate, after being washed with distilled water and alcohol, may be dried in an air oven at 100-110° C for an hour and weighed. In some experiments the precipitate of As_2S_5 was also washed with carbon bisulphide but no change in the weight of the precipitate was detected, thus showing that no precipitation of free sulphur takes place under the conditions of the experiment. The results are given in Tables I, II and III.

TABLE I

WITH $2N$ SODIUM SULPHIDE REAGENT (WASHING WITH ALCOHOL AND ETHER)

No.	Vol. of arsenate solution in ml	Vol. of reagent added in ml	Vol. of $12N$ HCl added in ml	Wt. of ppt As_2S_5 in g	Wt. of As in the ppt in g	Wt. of As actually present in g
1	25	10	35	0.0727	0.03508	0.03508
	25	10	35	0.0728	0.03512	
	25	9	34	0.0728	0.03512	
2	10	15	30	0.1303	0.06291	0.06298
	10	15	30	0.1304	0.06295	
	10	13	30	0.1305	0.06300	
3	25	20	50	0.2688	0.13007	0.12996
	25	20	60	0.2690	0.13017	
	25	20	50	0.2687	0.13000	

TABLE II

WASHING WITH WATER AND HEATING AT 100 — 110° C

No.	Vol. of arsenate solution in ml	Vol. of reagent added in ml	Vol. of $12N$ HCl added in ml	Wt. of ppt As_2S_5 in g	Wt. of As in the ppt in g	Wt. of As actually present in g
1	25	10	35	0.0726	0.03504	0.03509
	25	8	35	0.0727	0.03508	
2	10	15	30	0.1304	0.06295	0.06298
	10	15	30	0.1305	0.06300	
3	25	20	50	0.2688	0.13007	0.12996
	25	20	50	0.2689	0.13012	

TABLE III

WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT (WASHING WITH ALCOHOL AND ETHER)

No.	Vol. of arsenate solution in ml	Vol. of reagent added in ml	Vol. of $12N$ HCl added in ml	Wt. of ppt As_2S_5 in g	Wt. of As in the ppt in g	Wt. of As actually present in g
1	25	10	35	0.0728	0.03512	0.03509
	25	9	35	0.0727	0.03508	
	25	8	35	0.0727	0.03508	
2	10	15	30	0.1303	0.06291	0.06298
	10	13	30	0.1302	0.06288	
	10	14	30	0.1304	0.06295	
3	25	25	55	0.2688	0.13007	0.12996
	25	25	55	0.2690	0.13017	
	25	25	55	0.2690	0.13017	

Estimation of tellurium

Out of the two methods[5,6] so far recommended for the gravimetric estimation of tellurium only one has found a place in standard text books. This is based on the reduction of the acid solution to the metal with sulphur dioxide. The method, however, is considered unsatisfactory owing to the rapid oxidation by air of the precipitated tellurium as the following remark will show[5] "Reduction by sulphur dioxide alone is slow and the precipitate is so very finely divided that it oxidizes readily in spite of washing with alcohol and other". The precipitation of tellurium as TeS_2 by decomposing the thiosalt therefore provides for the first time a satisfactory and convenient method for its gravimetric estimation.

For estimating tellurium as TeS_2 a standard solution of tellurium was prepared by dissolving a weighed quantity of pure metallic tellurium (KAHLBAUM'S) in nitric acid, evaporating it almost to dryness on the water bath, and making up to a known volume in a measuring flask with a small quantity of caustic soda solution. Measured volumes of the sodium tellurite solution were treated with a large excess of approximately $5N$ ammonium or $2N$ sodium sulphide solution, about 10 ml of the alkali sulphide solution being required for every 50 mg of tellurium. The solution was then treated with sufficient excess of cold $2N$ hydrochloric acid to produce a concentration of about $1N$ hydrochloric acid in the resulting mixture. The precipitate was stirred, filtered through a weighed Gooch or sintered glass crucible (porosity 4), washed with distilled water, heated to 100-110° C in an air oven for half an hour, cooled in a vacuum desiccator and weighed. The weights of metallic tellurium contained in the measured portions of the solutions and those corresponding with the precipitate actually obtained are given in Table IV, and V.

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TABLE IV

WITH 2*N* SODIUM SULPHIDE REAGENT

No.	Vol. of Te solution in ml	Vol. of reagent added in ml	Vol. of 2*N* HCl added in ml	Wt. of ppt. TeS_2 in g	Wt. of Te in the ppt in g	Wt. of Te actually present in g
1	10	10	25	0.0970	0.06423	0.06420
	10	15	30	0.0971	0.06429	
	10	20	50	0.0970	0.06423	
2	25	15	40	0.1186	0.07905	0.07900
	25	20	50	0.1188	0.07920	
	25	15	50	0.1190	0.07930	
3	20	25	60	0.1942	0.12858	0.12840
	20	30	75	0.1941	0.12852	
	20	35	75	0.1942	0.12858	

TABLE V

WITH 5*N* AMMONIUM SULPHIDE REAGENT

No.	Vol. of Te solution in ml	Vol. of reagent added in ml	Vol. of 2*N* HCl added in ml	Wt. of ptt TeS_2 in g	Wt. of Te in the ppt in g	Wt. of Te actually present in g
1	10	15	50	0.0971	0.06429	0.06420
	10	15	40	0.0970	0.06423	
	10	20	50	0.0969	0.06416	
2	25	15	50	0.1186	0.07905	0.07900
	25	15	50	0.1190	0.07930	
	25	20	60	0.1186	0.07905	
3	20	25	75	0.1941	0.12852	0.12840
	20	30	90	0.1942	0.12858	
	20	35	100	0.1940	0.12846	

Estimation of selenium

A solution of sodium selenite was prepared and the exact quantity of selenium present in it was estimated in the usual way by precipitating the metal by means of sulphurous acid. Measured volumes of the standardized sodium selenite solution were treated with a large excess of approximately 5*N* ammonium sulphide or 2*N* sodium sulphide solution, about 5 ml of either alkali sulphide solution being required for every 50 mg of selenium. The solution was then acidified with sufficient quantity of 2*N* hydrochloric acid to produce a concentration of 1*N* hydrochloric acid in the resulting mixture. The required quantity of the acid should be added all at once and not drop by drop. In the former case an easily filterable orange coloured precipitate is obtained while in the latter a precipitate of selenium and sulphur appears successively as the concentration of the acid in the solution increases. The weight of the precipitate also, in the latter case, is too high. The orange coloured precipitate was filtered through a weighed Gooch or sintered glass crucible, washed with water, dried in an air oven at 100-110° C for half an hour, cooled in a desiccator and weighed. The weights of metallic selenium contained in the measured portions of the solution and those corresponding with the precipitate actually obtained are given in Tables VI and VII.

TABLE VI

WITH $2N$ SODIUM SULPHIDE REAGENT

No.	Vol. of Se solution in ml	Vol. of reagent added in ml	Vol. of $2\ N$ HCl added in ml	Wt. of ppt SeS_2 in g	Wt. of Se in the ppt in g	Wt. of Se actually present in g
1	10	5	15	0.0433	0.02383	0.02385
	10	10	20	0.0434	0.02388	
	10	8	25	0.0434	0.02388	
2	20	8	30	0.0867	0.04770	0.04770
	20	10	30	0.0868	0.04775	
	20	15	35	0.0868	0.04775	
3	25	8	35	0.0931	0.05142	0.05130
	9	4	15	0.0336	0.01849	0.01847
	25	15	40	0.0930	0.05136	0.05130

TABLE VII

WITH $5N$ AMMONIUM SULPHIDE REAGENT

No.	Vol. of Se solution in ml	Vol. of reagent added in ml	Vol. of $2N$ HCl added in ml	Wt. of ppt SeS_2 in g	Wt. of Se in the ppt in g	Wt. of Se actually present in g
1	10	8	40	0.0434	0.02388	0.02385
	10	4	30	0.0433	0.02383	
	10	6	35	0.0433	0.02383	
2	20	20	80	0.0867	0.04770	0.04770
	20	8	50	0.0868	0.04775	
	20	10	50	0.0867	0.04770	
3	25	10	50	0.1084	0.05960	0.05969
	25	8	50	0.1084	0.05960	
	25	15	60	0.1083	0.05955	

On washing the precipitate of tellurium and selenium sulphides with carbon disulphide or with alcohol and ether there is a progressive decrease in weight. This is probably due to the decomposition of the sulphide into the metal and sulphur and the solution of the sulphur (and also selenium) thus formed in the solvent. But if the precipitate is washed with water and dried at 100-110° C its weight corresponds exactly with the formula TeS_2 or SeS_2 and thus gives an exact estimate of the amount of tellurium or selenium present. Previous observers[7] who have studied the nature of the precipitate formed by passing hydrogen sulphide into an acid solution of selenite have also reported that the ratio of Se : S in the precipitate is 1 : 2. It should be noted that selenium and tellurium must be present in the form of selenite or tellurite. The method is not applicable to selenates and tellurates.

SUMMARY

1. It has been shown that the complete precipitation of arsenic sulphide (from arsenates) by decomposing the thiosalt provides a remarkably convenient and rapid method for its estimation which is in marked contrast to the tedious methods so far available for this purpose.

2. The method of precipitating the sulphide by decomposing the thiosalt is also applicable to the estimation of tellurium for which no perfectly reliable gravimetric method had so far been devised.

3. Selenium also can be estimated gravimetrically by this method and it provides a convenient alternative to the well-known method based upon reduction to the metal.

4. The precipitates obtained in the case of arsenic, tellurium, and selenium correspond to the formulae As_2S_5, TeS_2 and SeS_2, respectively.

RÉSUMÉ

1. Il est démontré que la précipitation du sulfure d'arsenic (à partir des arséniates), par décomposition du thiosel, constitue une méthode de dosage très pratique et rapide, contrairement à la méthode usuelle.

2. La méthode de précipitation du sulfure par décomposition du thiosel s'applique également au tellure, pour lequel il n'existe encore aucun dosage gravimétrique parfait.

3. Le sélénium peut aussi être dosé gravimétriquement par ce procédé.

4. Les formules des précipités obtenus avec l'arsenic, le tellure et le sélénium sont respectivement As_2S_5, TeS_2 et SeS_2.

On recommande d'utiliser soit cette précipitation comme sulfure soit la réduction en sélénium élémentaire.

ZUSAMMENFASSUNG

1. Es wurde gezeigt, dass die vollständige Ausfällung von Arsensulfid (aus Arsenaten) durch die Zersetzung des Thiosalzes eine beträchtlich bequeme und rasche Bestimmungsmethode darstellt im strengen Gegensatz zu den bis jetzt zu diesem Zweck üblichen langwierigen Methoden.

2. Die Methode zur Ausfällung der Sulfide durch Zersetzung der Thiosalze kann auch zur Bestimmung des Tellurs, für das bis jetzt noch keine vollkommen zuverlässige Methode ausfindig gemacht werden konnte, angewandt werden.

3. Selen kann ebenfalls durch diese Methode gravimetrisch bestimmt werden und die Methode gibt so eine bequeme Abwechslung mit der auf die Reduktion zum Metall begründeten wohlbekannten Methode.

4. Die im Falle des Arsens, bzw. Tellurs und Selens erhaltenen Niederschläge entsprechen der Formel As_2S_3 bzw. TeS_2 und SeS_2.

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ON THE VOLUMETRIC DETERMINATION OF HYDROGEN SULFIDE AND SOLUBLE SULFIDES

by

PER OLOF BETHGE

Swedish Forest Products Research Laboratory, Wood Chemistry Department, Analytical Laboratory, Stockholm (Sweden)

METHODS USING IODINE AS THE OXIDIZING AGENT

Most volumetric methods for the determination of hydrogen sulfide or soluble sulfides are based on the reaction

$$H_2S + I_2 = S + 2\,H^+ + 2\,I^-$$

which takes place in an acid medium. Iodometric titration of sulfides has been used widely for a long time, and many modifications of the method of titration are described in the literature. These fall into two main groups: 1) The sulfide is titrated directly with iodine or iodide — iodate mixture[1]. 2) An excess of iodine or iodide — iodate mixture is added, and the excess is back-titrated[2, 3].

When hydrogen sulfide is to be determined, it must be absorbed in a suitable absorbent before the volumetric determination. Many different absorbents have been proposed; the most popular seem to be buffered or ammoniacal solutions of zinc or cadmium salts, or sodium hydroxide solution. It will be shown later that the nature of the absorbent is of great importance for the precision and accuracy[9a] of the determination. Of the many sources of error reported, the chief seem to be:

1. Occlusion of iodine in the elementary sulfur formed; this iodine escapes the titration[2]. This error can be eliminated by dissolving the sulfur in carbon disulfide, but a better method is to disperse the sulfur colloidally by means of starch[4].

2. If the solution containing sulfide is acidified and then titrated with iodine, there is a risk that hydrogen sulfide will escape, especially when the sulfide content is high. The back-titration method avoids this drawback to some extent, but even when an alkaline sulfide solution is added to acidified iodine, there is some risk that hydrogen sulfide will be lost. A good method of avoiding these sources of error is to suck the sulfide solution into an evacuated flask.

3. In alkaline solution iodine oxidizes sulfide partially to sulfate. Hence if very alkaline solutions containing sulfide are added to acidified iodine, there is some risk of a minor part of the sulfide being oxidized to the sulfate state, especially if the iodide ion concentration is low.

4. Iodine may be lost by evaporation if the temperature of the solution is raised appreciately above room temperature. This may be the case when the absorbent is neutralized, but can be avoided by slow mixing and effective cooling.

5. Sulfides in alkaline media are oxidized by air. Experiments should be arranged so that alkaline absorbents containing sulfide have the minimum contact with air.

6. Cadmium sulfide is photosensitive, and when working with this absorbent the sulfide must be protected from light. Zinc sulfide is not photosensitive.

7. Hydrochloric acid, which has been in contact with air, and strong sulfuric acid may oxidize iodide ions to iodine. It should be ascertained, by adding potassium iodide and starch solution to the acid used for acidifying the absorbent, that no blue color appears. If a blue color appears, too much iodine will be present and the results will be low.

Experiments have confirmed the findings of SHAW[5] and KITCHENER *et al.*[6] that slight modifications in technique and method may produce great differences in the results. The critical point seems to be the mixing of the absorbent containing the sulfide with the iodine solution. If a sodium sulfide solution, prepared as described below, is pipetted directly into an acidified iodine solution, and the excess back-titrated with standard sodium thiosulfate, the results are highly reproducible, but if the sodium sulfide is first added to an absorbent containing cadmium or zinc and the mixture is added to the iodine, the results vary. If the absorbents without sulfide are added to the iodine solution, no change is obtained in the amount of thiosulfate consumed, compared with the iodine solution alone. The particle size of the sulfur is smallest when no absorbent is present, and becomes larger, the more alkaline the absorbent and the greater its ionic strength. It is conceivable that large sulfur particles include particles of cadmium or zinc sulfide besides some iodine.

Bearing the results of these experiments in mind, the following principles should be followed in iodometric determinations of sulfides: —

a. The sulfide in the absorbent should not form any precipitate.

b. The ionic strength of the absorbent should be kept as low as possible.

c. Air should be excluded.

d. The absorbent containing the sulfide should be added to the acidified solution before the addition of the iodine.

e. The heat of neutralization should be as low as possible.

The following method was worked out for determining the sulfide content of sulfide solutions or of those also containing sodium hydroxide.

Apparatus. A separating funnel, provided with glass standard tapered joints, a piece of glass tubing and an Erlenmeyer flask, also with standard tapered joints (Fig. 1).

Solutions. 0.1 or 0.01*N* iodine solution. It is not necessary to know the exact titer of this solution.

5*M* phosphoric acid. 342 ml of 85 per cent. phosphoric acid are diluted to one litre.

Starch solution, 0.2 per cent.

Procedure. 25 ml of phosphoric acid and 5 ml of starch solution are pipetted into the flask. The separating funel is connected and the apparatus is evacuated through the glass tubing. The stopcock is closed and the upper glass joint is disconnected. The sulfide solution is pipetted rapidly into the separating funnel, and the stopcock opened a little, so that the sulfide solution drops into the flask. The funnel is rinsed twice with 5 ml of water, cooled if necessary and a measured amount of iodine solution added in the same way as the sulfide. If the color of iodine disappears, more iodine solution must be added. After 2 minutes, the lower glass joint is disconnected and the solution titrated with standard thiosulfate until the last of the blue color disappears. A blank is run with the same amount of iodine solution.

Calculation. mg S = (blank — test) × thiosulfate titer × 16.03.

The precision is quite sufficient for ordinary analytical work, *cf.* Table I. Experiments have shown that the coefficient of variation* is of the order of 0.2 per cent.

To get a satisfactory test of the accuracy of the method is not easy, as there is no good standard for sulfides. The best method to be tried involved the preparation of pure sodium sulfide solution with complete exclusion of air. This was accomplished by dissolving sodium sulfide (analytical reagent) in freshly boiled distilled water, through which a stream of purified nitrogen gas was passed, mainly as described by KIRSTEN AND CARSTENS[7]. In order to remove oxygen from ordinary cylinder nitrogen, the gas was first passed through an electrically heated tube containing active copper, as described by MEYER AND RONGE[8]. Equal amounts of this solution were either titrated as described or oxidized to sulfate by hydrogen peroxide. The oxidation was carried out as follows: 100 ml of sodium sulfide solution were added to ammoniacal hydrogen peroxide (5 ml "Perhydrol" and 10 ml ammonium hydroxide) in a "Vycor" glass flask. The excess of peroxide was destroyed by boiling, the solution was acidified with a few drops

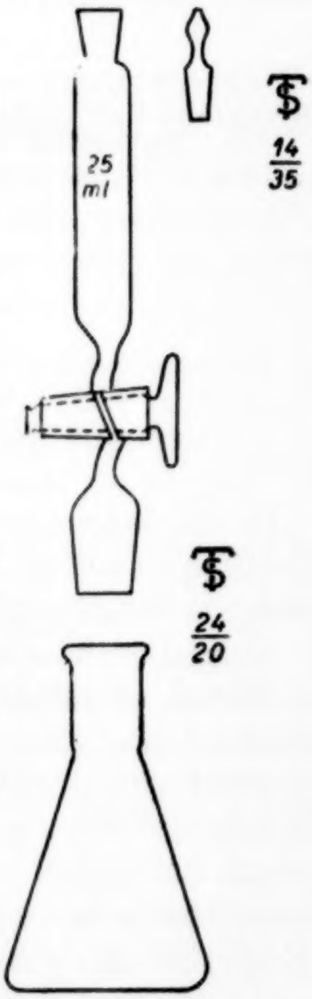

Fig 1. The apparatus

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* Standard deviation divided by the mean value.

of hydrochloric acid and evaporated to dryness. The material was dissolved in water, the solution was filtered and barium chloride added. The precipitate was collected after two hours, washed, ashed, and ignited. Tests showed that the precipitate did not contain significant amounts of silica. From the weight of the barium sulfate, the amount of sulfur in 100 ml sulfide solution was calculated.

The results of these experiments are shown in Tables I and II.

TABLE I

MILLIGRAMS OF SULFUR FOUND, BY THE TITRATION METHOD, IN 10 ML OF SODIUM SULFIDE SOLUTION

1.977	Mean value: 1.983 mg of S
1.981	Standard deviation: 0.0041 mg
1.980	Coefficient of variation: 0.21 %
1.983	
1.988	
1.988	
1.981	

TABLE II

MILLIGRAMS OF SULFUR FOUND, BY THE BARIUM SULFATE METHOD, IN 100 ML OF THE SAME SODIUM SULFIDE SOLUTION AS IN TABLE I

19.89	Mean value: 19.885 mg of S
19.88	Standard deviation: 0.035 mg
19.83	Coefficient of variation: 0.18%
19.82	

METHODS USING SODIUM HYPOCHLORITE AS THE OXIDIZING AGENT

In the iodometric methods for the determination of sulfides, the sulfide is oxidized to sulfur. In methods in which the sulfide is oxidized to sulfate, four times as much oxidant is required, and so the sensitivity is increased fourfold.

Several authors have proposed the use of sodium or calcium hypochlorite for oxidation of sulfide to sulfate [6, 9, 10, 11, 12]. In all these methods the sulfide is oxidized in an alkaline medium with an excess of hypochlorite, which is then back-titrated with thiosulfate after the addition of potassium iodide and acidification. KOLTHOFF[9] does not give any precise information about the conditions under which the oxidation is to be performed. KITCHENER *et al.*[6] propose 0.1*N* sodium hypochlorite in 0.4*N* sodium hydroxide for absorption, and oxidation at 100° C. KIRSTEN[10] uses 4 ml of a *ca.* 25 per cent. sodium hydroxide solution for absorption and adds 3 ml sodium hypochlorite solution in 25 per cent. sodium hydroxide for the oxidation, which is performed at room temperature. The strength of the hydroxide during the oxidation is thus *ca.* 6.2*N*. DUNICZ *et al.*[11] propose hypochlorite in 2.5*N* potassium hydroxide for absorption and oxidation.

Many estimations of hydrogen sulfide, absorbed in sodium hydroxide, with the aid of hypochlorite, have been made in this laboratory. It became obvious that the yield was not always the theoretical given by the equation:

$$S^{-2} + 4\,OCl^- = SO_4^{-2} + 4\,Cl^-.$$

To give a general impression of how the temperature and hydroxide concentration influenced the yield, the following experiment is given as a typical representative for a great number of titrations of this type.

Blank determinations were first made (Table III). To 25 ml portions of a sodium hypochlorite solution in 0.4*N* sodium hydroxide were added various amounts of 10*N* sodium hydroxide to obtain hypochlorite solutions of different alkalinity. Then 10 ml of water were added. Some of the solutions were now boiled for five minutes. After cooling 1 gram of potassium iodide was added and the solution was acidified. The liberated iodine was titrated with 0.1*N* standard sodium thiosulfate solution. Table IIIa shows that sodium hypochlorite decomposes when it is boiled in 5*N* hydroxide solution.

The main titrations (Table IIIb) were performed in the same way as the blanks, but 10 ml portions of sodium sulfide solution (*cf.* page 131) instead of the water, were pipetted into the solutions. When the sulfide was oxidized at 20° C, a white precipitate of sulfur was obtained if the hydroxide concentration was below 3*N*.

In Table IIIc the differences between corresponding mean values are listed.

TABLE III

IIIa. BLANK TITRATIONS: 25 ml NaClO in 0.4*N* NaOH + *a* ml 10*N* NaOH + 10 ml H_2O. *V* ml $Na_2S_2O_3$ 0.1*N* used in the titration

Oxidized at 20° C:	C_{OH^-}	0.4	1.0	2.5	5.0
	a	0.41	2.3	10.3	33
	V	24.24 24.22 24.21 24.21	24.12 24.14 24.17	24.03 24.07 24.09	24.02 23.95 24.04
	Mean	24.22	24.14	24.06	24.00
Oxidized at the boiling point for 5 minutes:	C_{OH^-}	0.4	1.0	2.5	5.0
	V	24.11 24.09 24.08	25.05 23.99 23.95	23.95 23.99 23.91	22.70 23.26
	Mean	24.09	24.00	23.95	(22.98)

IIIb. MAIN TITRATIONS: 25 ml NaClO in 0.4N NaOH + a m 10N NaOH + 10 ml Na_2S. V ml $Na_2S_2O_3$ used in titration

Oxidized at 20° C:	C_{OH^-}	0.4	1.0	2.5	5.0
	a	0.41	2.3	10.3	33
		16.00	13.70	11.90	11.73
	V	15.39	14.16	11.90	11.71
		15.60	13.89	11.92	11.74
					11.70
	Mean	15.66	13.90	11.91	11.72
Oxidized at the boiling point for 5 minutes:		12.32	11.93	11.75	11.05
	V	12.30	11.89	11.80	11.16
		12.33	11.90	11.77	
	Mean	12.32	11.91	11.77	11.11

IIIc. Ml 0.1N $Na_2S_2O_3$ consumed by 10 ml Na_2S

C_{OH^-} temp.	0.4	1.0	2.5	5.0
20°	8.56	10.24	12.15	12.28
100°	11.77	12.09	12.18	11.87

IIId. Ml 0.1N $Na_2S_2O_3$ consumed by 50 ml Na_2S, by the iodine method

	Blank.	Main test	Difference
	21.82	6.33	
	21.83	6.35	
	21.83	6.34	
	21.84	6.35	
Mean:	21.83	6.34	15.49

15.49 ml correspond to $\frac{15.49 \times 10 \times 4}{50}$ = 12.39 ml thiosulfate solution by the hypochlorite methods.

The figures give the relative amounts of sulfide determinated. At room temperature much lower values are obtained when the hydroxide content is low, due to incomplete oxidation and formation of sulfur.

The same sulfide solution as used in IIIb was also titrated by the iodine method described on page 131. The figures obtained are listed in Table IIId. From the values obtained, the quantity of thiosulfate solution which had to be used in the hypochlorite titrations to get the same yield was calculated.

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IIIe. Yield in per cent. of that obtained by the iodine method

C_{OH^-} temp.	0.4	1.0	2.5	5.0
20°	69%	82.6%	98.1%	99.1%
100°	95%	97.6%	98.3%	96%

In Table IIIe the yield obtained by the hypochlorite titrations are expressed as a percentage of the yield obtained by the iodine method. The yield never reaches 100 per cent., but rises with rising temperature and alkalinity. However, at 100° C and a hydroxide concentration of $5N$, the yield is only 95 per cent., due to the decomposition of the hypochlorite.

It may be concluded that hypochlorite methods for volumetric determination of sulfides have high sensitivity and precision if suitable conditions are chosen for oxidation, but the accuracy is not very great. When methods of this kind are used, the results ought to be multiplied by an empirical factor, the magnitude of which is governed by the oxidative conditions.

METHODS USING POTASSIUM PERMANGANATE AS THE OXIDIZING AGENT

Alkaline permanganate solution is a much stronger oxidant than the acid permanganate commonly used, and it has been proposed to use it for the oxidation of sulfides to sulfate in methods where the excess of permanganate is back-titrated with oxalic acid[13]. In alkaline media the permanganate itself, however, is reduced from the heptavalent state to the hexavalent or tetravalent state instead of the divalent state, as in acid media. The reduction products of the permanganate are strongly colored and the end point of a direct titration cannot be observed. An excess of permanganate must be used and this has to be back-titrated after acidification. The back-titration is easily performed with standard sodium thiosulfate solution, if potassium iodide is added to the acidified solution.

Experiments were made to discover whether sulfides could be estimated by a titration, using alkaline permanganate as the oxidant. Sodium sulfide solution was added to alkaline potassium permanganate solution. The violet color of the permanganate thereby turned green and, if more sulfide were added, a brown precipitate was formed. After acidification with dilute sulfuric acid and addition of potassium iodide, the excess of permanganate could be determined by titration with thiosulfate solution.

Some experiments of this kind were carried out with constant amounts of permanganate and varying amounts of sodium sulfide solution. In Fig. 2 the thiosulfate titration readings are plotted against the amounts of sulfide solution which were added. The slope of the curve so obtained is constant from 0 to 16.6 ml sulfide solution added, and then decreases. The point where the curve changes

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its slope corresponds to 3/5 of the blank reading (ml Na_2S = 0). From this experiment it is obvious that sulfides in alkaline media reduce permanganate ions to the tetravalent state. The lower part of the curve was calculated on the assumption that the rest of the sulfide was used up by the iodine liberated later in the titration process, according to the equation:

$$H_2S + I_2 = S + 2\,H^+ + 2\,I^-.$$

That this really happens was proved by the observation of the formation of sulfur in the titration flask when the amount of sulfide solutions exceeded 16.6 ml. This experiment demonstrates that it is not possible to titrate more sulfide than that corresponding to 3/5 of the blank reading.

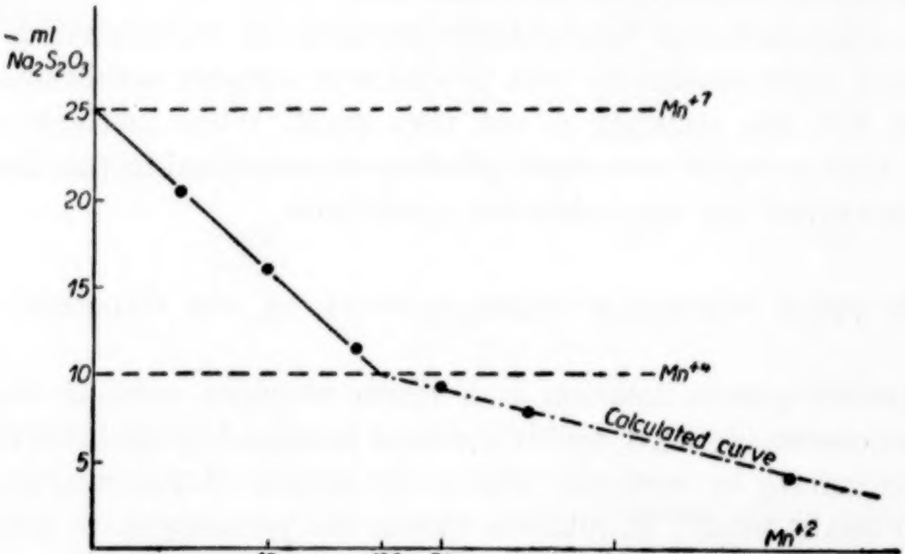

Fig. 2. Titrations with constant amounts of permanganate and varying amounts of sodium sulfide. Thiosulfate titration readings are plotted against the amounts of sulfide solution added.

Experiments analogous to those tabulated in Table III were carried out with permanganate solution. The blank titrations are found in Table IVa. Here 25 ml portions of a potassium permanganate solution were made alkaline by means of *a* ml of 10*N* sodium hydroxide solution. 10 ml of water were added and after five minutes the solution was acidified and titrated with standard sodium thiosulfate immediately after the addition of a few potassium iodide crystals. Half of the solutions were boiled for five minutes and cooled, before addition of acid. It is clear that strongly alkaline permanganate solutions are decomposed when boiled.

The main titrations, Table IVb, were performed in the same way as the blanks, but instead of the water 10 ml of sodium sulfide solution were added. The experiment was not made with the most alkaline solution at the boiling point.

In Table IVc the differences between the mean value of blank and main titrations are listed.

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TABLE IVa

25 ml 0.1*N* $KMnO_4$ + *a* ml 10*N* NaOH + 10 ml H_2O. *V* ml 0.1*N* $Na_2S_2O_3$ used in the titration

Oxidized at 20° C:	C_{OH^-}	0.4	1.0	2.0	5.0
	a	1.45	3.9	8.8	35
	V	24.90 24.92 24.90 24.87	24.85 24.89 24.87	24.74 24.72	23.99 23.98
	Mean	24.90	24.87	24.73	23.99
Oxidized at the boiling point for 5 minutes:	*V*	24.74 24.76 24.80	24.73 24.79	24.29 24.18	21.35 21.43
	Mean	24.77	24.76	24.24	21.39

TABLE IVb

Main titrations. 25 ml 0.1*N* $KMnO_4$ + *a* ml 10*N* NaOH + 10 ml Na_2S. *V* ml 0.1*N* $Na_2S_2O_3$ used in the titration

Oxidized at 20° C:	C_{OH^-}	0.4	1.0	2.0	5.0
	a	1.45	3.9	8.8	35
	V	12.81 12.83	12.78 12.80	12.74 12.75	12.56 12.43
	Mean	12.82	12.79	12.75	12.50
Oxidized at the boiling point for 5 minutes:	*V*	12.85 12.88	12.66 12.67	12.65 12.69	— —
	Mean	12.87	12.67	12.67	—

TABLE IVc

ml 0.1*N* $Na_2S_2O_3$ consumed by 10 ml Na_2S

C_{OH^-} temp.	0.4	1.0	2.0	5.0
20°	12.08	12.08	11.98	11.99
100°	11.90	12.09	11.57	—

In Table IVd the amounts of sulfur found are given as a percentage of that found in simultaneous titrations by the iodine method. As in the hypochlorite titrations, the yield never reaches 100%, or the theoretical.

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TABLE IVd

Yield in per cent. of the yield obtained by the iodine method				
c_{OH^-} temp.	0.4	1.0	2.0	5.0
20°	97.5	97.5	96.7	92.7
100°	96.0	97.6	93.4	—

SUMMARY

I. Common sources of error in the iodometric methods for the determination of hydrogen sulfide and soluble sulfides are discussed. An improved method for the iodometric determination is described and its precision and accuracy are discussed.

II. The volumetric determination of sulfides by means of alkaline hypochlorite solutions is discussed. It is concluded that the sensitivity is high, as is the precision when suitable oxidation conditions are chosen, but that the accuracy is not so high. The results must be multiplied by an empirical factor.

III. The determination of sulfides by means of alkaline potassium permanganate is discussed. The sensitivity is not as high as in the hypochlorite methods, because of the great excess of permanganate required. The precision is high if suitable oxidation conditions are chosen. As in the hypochlorite methods the accuracy is not high.

The iodine method is the most accurate, and this method ought to be used in cases where the greatest sensitivity is not necessary. In micro determinations, however, the hypochlorite method is in many cases the only solution to the problem, and in serial determinations the introduction of the empirical factor should produce results of great accuracy.

RÉSUMÉ

I. Les sources d'erreur habituelles dans le dosage iodométrique de l'hydrogène sulfuré, ainsi que des sulfures solubles dans l'eau, sont discutées. Une méthode perfectionnée de dosage iodométrique est décrite, dont la précision et l'exactitude sont discutées.

II. Le dosage volumétrique des sulfures, au moyen d'une solution d'hypochlorite alcalin, est exposé. Il est montré que la sensibilité et la précision, dans des conditions appropriées d'oxydation, sont élevées. Par contre l'exactitude n'est pas aussi bonne. Les résultats doivent être multipliés par un facteur empirique.

III. Le dosage volumétrique des sulfures, au moyen d'une solution de permanganate de potassium, est donné. La sensibilité n'est pas aussi bonne que celle obtenue lors du dosage à l'hypochlorite, en raison de l'excès de permanganate nécessaire. Ici également l'exactitude n'est pas aussi bonne que lors du dosage iodométrique.

La méthode de dosage iodométrique est à recommander lorsqu'une grande sensibilité n'est pas requise. Au contraire lors du micro-dosage, la méthode à l'hypochlorite est à préférer. Des résultats très exacts ont été obtenus lors d'un dosage en série, en faisant intervenir un facteur empirique.

ZUSAMMENFASSUNG

I. Die gewöhnlichen Fehlerquellen bei den jodometrischen Bestimmungsmethoden für Schwefelwasserstoff und wasserlösliche Sulfide, werden diskutiert. Eine

References p. 139.

verbesserte Methode für die jodometrische Bestimmung wird beschrieben und ihre Zuverlässigkeit und Genauigkeit wird diskutiert.

II. Die volumetrische Bestimmung von Sulfiden mit Hilfe von alkalischer Hypochloritlösung wird diskutiert. Es wird klargelegt, dass ihre Empfindlichkeit und Zuverlässigkeit bei zweckmässigen Oxydationsbedingungen gross ist, dass aber die Genauigkeit nicht so gross ist. Die Resultate müssen mit einem empirischen Faktor multipliziert werden.

III. Die volumetrische Bestimmung von Sulfiden mit Hilfe von alkalischer Kaliumpermanganatlösung wird diskutiert. Die Empfindlichkeit ist nicht so gross wie die der Hypochloritmethode, weil ein grosser Überschuss an Permanganat nötig ist. Die Zuverlässigkeit ist gross bei geeigneten Oxydationsbedingungen. Die Genauigkeit ist wie bei der Hypochloritmethode nicht gross.

Die Methode, bei welcher mit Jod oxydiert wird, ist die genaueste, und sie ist zu empfehlen, wenn grössere Empfindlichkeit nicht nötig ist. Bei Mikrobestimmungen dagegen ist die Hypochloritmethode oft die einzige Lösung, und bei Serienbestimmungen erhält man durch die Einführung eines empirischen Faktors sehr genaue Resultate.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURES OF SULFONAMIDES. VI

by

P. L. DE REEDER

Zwijndrecht (Netherlands)

QUANTITATIVE ANALYSIS

Since 1935, a rather large number of papers have been published concerning the various methods for the quantitative analysis of sulfonamides. They deal mainly with the determination of the more or less pure simple compounds, while only a minor part concerns mixtures of two or more sulfonamides. As in this investigation it has been our aim to develop general methods that are applicable to all mixtures to-day in common therapeutic use, these last-named papers were only of limited value to us, since they are always discussing one or more particular mixtures.

The treatment of some general methods for the quantitative analysis in this and forthcoming papers will be divided into the following parts:

I. Quantitative analysis of a mixture without previous separation of the components.
   A. Gravimetric and titrimetric methods.
   B. Colorimetric methods.
II. Quantitative analysis of a mixture after previous separation of the components.

The treatment of IA will form the main part of the following discussion, while IB and II were not studied by us in great detail.

I. QUANTITATIVE ANALYSIS OF A MIXTURE WITHOUT PREVIOUS SEPARATION OF THE COMPONENTS

A. Gravimetric and titrimetric methods

These "classical" methods have long been applied to the determination of simple sulfonamides. Their use in the analysis of a mixture depends on the following principle.

We consider a mixture of *n* components, called 1, 2, 3 . . . *n*. The percentage of each of these compounds in the mixture is assumed to be x_1, x_2, x_3 . . . x_n. These *n* unknowns can now be solved from a set of *n* equations, which are set up as follows.

1) In the mixture, the *total* quantity of some element or group, symbolized by E_1 (Na, aromatic NH_2, SO_2NH_2, etc.), is determined. From this quantity the percentage of some component cannot be calculated, unless only *one* compound contains the particular element or group under consideration. We shall assume this not to be the case. Therefore, we can only say that

$$\frac{a.x_1}{100.M_1}(E_1)_1 + \frac{a.x_2}{100.M_2}(E_1)_2 + \frac{a.x_3}{100.M_3}(E_1)_3 + \ldots\ldots + \frac{a.x_n}{100.M_n}(E_1)_n = e_1$$

where a = weighed quantity of the mixture;
e_1 = quantity of some element or group E_1 found;
M_p = molecular weight of component $p (p = 1, 2, 3, \ldots \text{ or } n)$;
$(E_1)_p$ = gram E_1 present in one mol p.

2) In the same way, the determination of the quantity of a second element or group (called E_2) gives

$$\frac{b.x_1}{100.M_1}(E_2)_1 + \frac{b.x_2}{100.M_2}(E_2)_1 + \ldots\ldots + \frac{b.x_n}{100.M_n}(E_2)_n = e_2$$

(The signification of the symbols is the same as in equation 1.)

3) ....

n) At last, the determination of the quantity of E_n gives

$$\frac{r.x_1}{100.M_1}(E_n)_1 + \frac{r.x_2}{100.M_2}(E_n)_2 + \ldots\ldots + \frac{r.x_n}{100.M_n}(E_n)_n = e_n$$

n+ 1) If one is certain that in setting up the above equations *all* compounds of the mixture have been taken into account, there can finally be written

$$x_1 + x_2 + x_3 + \ldots\ldots + x_n = 100.$$

This equation may be used to check the results of the determinations; it may also take the place of one of the above equations. The latter is not advisable, however, since then there is no check at all to the results found.

To solve the set of equations the following data must thus be known.

a) The quantities M_p and $(E_1)_p$, $(E_2)_p$, etc. This means, that the identity of the components have to be known. This has been amply discussed in the preceding papers.

b) The quantities e_1, e_2, etc. This depends on having suitable methods for the determination of certain elements or groups in the sulfonamide-molecule. We shall occupy ourselves with this problem in this and the following papers.

The determination of the following elements and groups will be discussed:

I) The determination of the total amount of carbon and hydrogen.
II) The determination of the total amount of nitrogen.
III) The determination of the total amount of sulfur.
IV) The bromometric titration of the whole molecule.
V) The nitrite titration of the free aromatic amino group.
VI) The gravimetric and titrimetric determinations of the SO_2NH-group.
VII) The gravimetric and titrimetric determinations of the aromatic amino group.
VIII) The determination of the amidic –NH–R–groups.
IX) The determination of the total amount of sodium.

I. Determination of the total amount of carbon and hydrogen in the mixture

The well-known combustion analysis after LIEBIG (modified in a great variety of ways) forms an indispensable part in the determination of the composition of newly prepared substances or unknown isolated compounds. It has seldom or never been used, however, in the determination of known compounds, and this for the following two reasons:

a) The compounds that are present in addition to the one to be determined are mostly also organic compounds and are thus included in the determination.

b) The performance of the determination requires a rather extensive apparatus and some routine in carrying out the analysis. The latter especially applies to the performance on semi-micro or micro-scale.

In our mixtures of sulfonamides, however, the first point mentioned has another aspect. The *number* and the *identity* of the compounds present have been established by the previous qualitative analysis. Since we are dealing with pharmaceutical products, we may also assume a reasonable degree of purity. The presence of "foreign admixtures" can be neglected then.

We refer to one of the restrictions mentioned in our first paper. It was assumed there that the mixtures investigated did not contain any other compounds besides sulfonamides. If this is not the case here, either the nature of these compounds must be established, or they must be removed quantitatively (without alteration of the composition of the rest of the mixture) before a quantitative analysis is carried out. This forms an apart investigation, of course.

The second objection, that of apparatus and experimental complexity, remains, however. This restricts the application of the method to the laboratories that are properly equiped for this purpose. Since our private laboratory, in which the investigation was carried out, did not belong to this group, we ourselves were not able to study this method of analysis. There can hardly be doubt, however, that it can be applied to all sulfonamides under discussion, the method being a universal one.

Fortunately, there remain sufficient elements and atomic groups in the sulfonamide-molecule that can be determined in easier ways.

II. The determination of the total amount of nitrogen in the mixture

A. The determination of nitrogen after Dumas resembles the preceding determination of C and H in apparatus and experimental difficulties, and in the conditions concerning purity and composition of the mixture. It is also a determination which is seldom used in the quantitative analysis of a mixture, but which, like the previous one, might be of value if other determinations fail.

B. The determination of nitrogen by means of the Kjeldahl method requires a less extensive apparatus than Dumas' method and yet will produce very good results with most of the sulfonamides under consideration. If has often been stated in the literature that, generally, nitrogen bound in heterocyclic rings, in nitro-, nitroso- and N = N-groups, etc., cannot be determined with the aid of the Kjeldahl method. In fact, the therapeutically important heterocyclic derivates of sulfanilamide form an exception to this rule, since their nitrogen can be determined very effectively in this way. This has been verified experimentally by Lapière[2,3,24], Schuleck and Rosza[5] and Chapman and Pierce[76]. Their results can be summarized as follows.

The compounds that can be determined without a previous treatment are

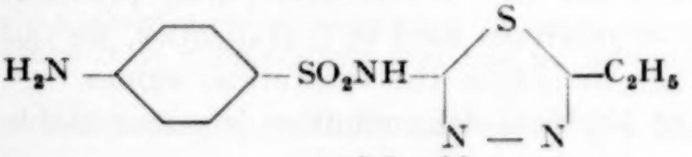
sulfanilamide
sulfacetamide
sulfapyridine
sulfathiazole
sulfadiazine
sulfamerazine
sulfamezathine
septazine.

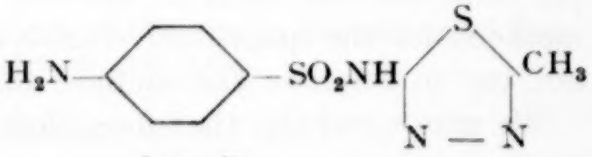
A compound giving only good results after previous hydrogenation is prontosil soluble (an azo-sulfonamide which was briefly mentioned in our first paper).

No correct values are obtained with:

soluseptazine[73]
globucid[3]

Globucid and lucosil are two sulfas of less therapeutic importance and are not discussed in our papers.


globucid


lucosil

Since this method can thus very readily be used to determine one of the quantities e_1, e_2, etc., indicated above, we shall discuss some details of its performance.

A very important feature of the determination is the right choice of the destruction mixture. In general it must be stated that the sulfonamides are highly resistant to complete oxidation and destruction. LAPIÈRE[2] has found a destruction mixture that proved to be satisfactory with a large number of various sulfonamides. However, also with this mixture the destruction must be called time-consuming if it is compared with the destruction times usually met with in other compounds. In our investigations LAPIÈRE's method was used without alteration.

In a small Kjeldahl-flask (100 ml) are placed 100-200 mg of the sulfonamide-mixture, 10 ml of concentrated sulfuric acid, 500 mg of anhydrous zinc sulfate and 500 mg of anhydrous copper sulfate. The mixture is heated to boiling. Every three minutes it is cooled a little, after which 4-5 drops of hydrogen peroxide (30%) are added. Boiling is then continued.

Destruction is complete after 3-4 hours. The ammonia is then determined in the usual way (steam-distillation after addition of alkali).

A new method is the direct titration of NH_4-ions in the destruction liquid, using formaldehyde and alkali[77]. Distillation is thus avoided. We did not use this method in our sulfonamide-investigations, but applied it in the Kjeldahl determinations of nitrogen in certain proteins, where it gave us highly satisfactory results. Since this method is very rapid also, its use can be highly recommended here.

Using this method we obtained the following results with some pure sulfonamides of which Kjeldahl-determinations have not been reported in the literature (Table IX).

TABLE IX

Compound	% N calcd.	% N found	
Elkosin	20.1	19.8	19.7
Irgafen	9.2	9.1	9.1
Irgamid	11.0	10.8	10.9
Sulfamethylthiazole	15.6	15.3	15.5
Succinylsulfathiazole	11.8	11.6	11.5
Na-sulfadiazine	20.6	20.7	20.5
Na-sulfamerazine	19.6	19.3	19.4
Na-sulfamezathine	18.7	18.4	18.6

Figures given in Table IX are very satisfactory, being mostly only one or two per cent. too low. Since it has only been our aim to elaborate purely practical methods for the quantitative analysis of mixtures used in therapeutics, we did not try to improve the method further to obtain the theoretical values.

We may conclude, therefore, that the Kjeldahl determination is very suitable to the analysis of the nitrogen-content of pure sulfonamides.

As to the application to mixtures: difficulties are hardly to be expected here. This may further be proved from the data in Table X; the mixtures listed there were prepared from the pure, previously well dried, compounds by weighing the amounts indicated in one weighing-bottle and hereafter mixing them by shaking.

TABLE X

Compounds	Weight in g	% N calcd.	% N found	%
Sulfadiazine	0.5328			
Sulfamerazine	0.4173	21.2	20.8	98.0
Sulfamezathine	0.5781		20.9	98.4
Sulfathiazole	0.8037	19.0	19.1	100.2
Sulfadiazine	0.6411		18.8	98.8
Sulfamethylthiazole	0.5328		17.4	98.7
Sulfathiazole	0.6722	17.6	17.7	100.5
Sulfamerazine	0.5036		17.5	99.3
Elkosin	0.7308	16.1	15.9	98.6
Succinylsulfathiazole	0.6921		15.9	98.6

LAPIÈRE *et al.*[21] estimated the nitrogen-content of a mixture of sulfadiazine, sulfathiazole and sulfamerazine; they found 19.54%, while 19.78% was calculated, so 98.6% was recovered. These data agree well with the ones given in Table X.

Difficulties will be encountered, of course, if one of the following sulfonamides is present in the mixture: prontosil soluble, soluseptazine or globucid (*cf.* above). Since these compounds are seldom encountered in to-day's practice, however, we did not investigate this difficulty in more detail. These compounds will seldom (if ever) be encountered in mixtures.

The hydrogenation of prontosil soluble previous to the Kjeldahl determination has been investigated by LAPIÈRE[2].

III. The determination of the total amount of sulfur in the mixture

This element is usually estimated by complete oxidation of the organic compound(s), whereby the sulfur is transformed into sulfate, which then is gravimetrically or titrimetrically determined.

For the oxidation, a number of various methods is available; they can be divided into two groups:

A. Oxidation by melting with oxidizing compounds.

B. Oxidation in solution.

C. A third method: oxidation by gaseous oxygen or chlorine is not discussed here, since it is cumbersome and has no advantages in our case.

We first give a short survey of the literature.

A. Oxidation by melting with oxidizing compounds.

This method has been amply investigated by LAPIÈRE[2,24]. In his mode of operation melting was always performed after mixing the sample with a mixture of sodium-potassium-carbonate and potassium nitrate (1:1). Performance: 0.1-0.5 g of the sample is mixed in a porcelain crucible with 2-3 g of this oxidation-mixture, and the mass covered with another layer of the latter. The crucible is heated with a small flame for half an hour; hereafter, the flame is enlarged very carefully till the mass has melted completely. After cooling the mixture is dissolved in boiling water, the solution filtered and the filter paper washed with boiling water until the filtrate is no more alkaline. The filtrate is acidified with hydrochloric acid (10%) and evaporated to a small volume on a water-bath (in this way, the main part of the nitric acid is removed). The sulfate is then determined with barium chloride in the usual way.

This method has given excellent results with all sulfonamides which were investigated by LAPIÈRE: sulfadiazine, sulfamerazine, sulfamezathine, sulfathiazole, sulfapyridine, sulfanilamide, septazine, prontosil soluble and rodilone.

B. Oxidation in solution.

For the sulfa's, different modes of operation have been published. The following liquids have been used as oxidizing agents:

H_2O_2 and $FeCl_3$, next HCl and $NaNO_2$[78];
Br_2 and concentrated HCl[79];
H_2O_2 and concentrated HCl[80];
H_2O_2 and concentrated HNO_3[5,81];
$KMnO_4$ and K_2CO_3[42,47];
$KMnO_4$, HNO_3 and HCl[82].*

In these investigations good results were obtained with sulfathiazole[5,47], sulfapyridine[5,42], sulfanilamide[5,80], sulfacetamide, sulfamethylthiazole, ulirone, neo-ulirone and prontosil soluble (all[5]) (the latter three being of only limited therapeutic value to-day).

This list is not a complete one, since some original papers could not be consulted, while the Chemical Abstracts did not supply sufficient information.

LAPIÈRE[2] proved that in the performance after VON MIKO[80] the oxidation is not a complete one, part of the sulfur not being oxidized to sulfate.

As the dry oxidation method of LAPIÈRE seemed to be the fastest and most convenient one, which, moreover, had been investigated thoroughly on its reliability by the author, we have chosen it for our further investigation.

The following pure compounds were first analysed (Table XI).

In assaying the sodium salts it proved advantageous to keep the mixture for some time at the melting temperature. Otherwise the figures obtained will be somewhat too low.

There was, of course, hardly any doubt that the method was suitable to the analysis of mixtures of sulfa's. One example has been found in the literature:

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* Here, the sulfate is precipitated as benzidine-sulfate and next titrated. All other methods employ the $BaSO_4$-precipitation.

TABLE XI

Compound	% S calcd.	% S found	
Elkosin	11.5	11.1	11.1
Irgafen	10.5	10.3	10.2
Irgamid	12.6	12.5	12.3
Sulfamethylthiazole	23.8	23.5	23.7
Succinylsulfathiazole	18.0	17.9	18.0
Na-sulfadiazine	11.8	11.5	11.6
Na-sulfamerazine	11.2	11.1	11.0
Na-sulfamezathine	10.7	10.5	10.5

Lapière and Lenaers[24] determined the sulfur-content of a mixture of sulfathiazole, sulfadiazine and sulfamerazine. They found 16.88% S, while 17.16% was calculated (= 98.3%).

Our determination of some self-made mixtures are listed in Table XII.

TABLE XII

Compound	Weight in g	% S calcd.	% S found		%	
Sulfadiazine Sulfamezathine Sulfamerazine	0.4729 0.5084 0.4561	12.2	12.1	12.0	99.0	98.4
Sulfathiazole Sulfamerazine	0.6332 0.6540	18.6	18.3	18.4	98.3	98.6
Sulfamethylthiazole Rodilone	0.8239 0.4226	19.1	18.7	19.0	97.8	99.4
Sulfanilamide Sulfapyridine	0.6243 0.7539	15.5	15.3	15.2	98.5	98.0

It appears that the determination of the sulfur-content according to the method described is completely satisfactory for practical purposes.

With the aid of the Kjeldahl-determination of nitrogen and the sulfur determination, the composition of a mixture of two sulfonamides can quantitatively be evaluated. However, if there are more compounds present more data must be at hand to solve the appropriate set of equations. In our seventh paper we will discuss two determinations in common use, and therefore of high importance: the bromatometric and the nitrite titration of the sulfonamide molecule.

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SUMMARY

The estimation of the quantitative composition of a mixture of sulfonamides can be performed without previous separation of the components, nor is it necessary to use reactions that are strictly specific for one component either. The unknown percentages are calculated from a set of equations, which can be solved if the total quantities of some elements or atomic groups, present in the compounds making up the mixture, have been determined.

In this paper, the determination of the total amounts of C, H, N and S are discussed, the latter two in more detail.

RÉSUMÉ

La détermination de la composition quantitative d'un mélange de sulfamidés peut être exécutée sans séparation préalable des composés. On n'a pas besoin non plus de réactions spécifiques pour chaque composé. Les pourcentages inconnus sont calculés au moyen d'un système d'équations. Ce système peut être résolu après détermination quantitative de quelques éléments ou groupes atomiques, présents dans les composés formant le mélange.

Dans ce mémoire, on discute les méthodes de dosages de C, H, N et S (les deux derniers de façon plus détaillée).

ZUSAMMENFASSUNG

Die quantitative Bestimmung der Zusammensetzung einer Mischung von Sulfonamiden kann ausgeführt werden ohne vorhergehende Trennung der Komponenten. Die Benutzung einiger Reaktionen, welche spezifisch sind für jede der Verbindungen der Mischung, ist ebensowenig notwendig. Die unbekannten Prozentsätze werden berechnet mit Hilfe von einem Gleichungensystem, das gelöst werden kann nach die Bestimmung der totalen Menge einiger Elementen oder Atomgruppen in den Verbindungen der Mischung.

In dieser Mitteilung werden die Bestimmungen von C, H, N und S besprochen, die beiden Letzten etwas mehr eingehend.

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APPLICATION DE LA CHROMATOGRAPHIE SUR ÉCHANGEUR D'IONS À L'ÉTUDE DE LA COMPOSITION DES ALIMENTS EN ACIDES AMINÉS*

par

E. SCHRAM, J. P. DUSTIN, S. MOORE** ET E. J. BIGWOOD

Laboratoire de Biochimie, Faculté de Médecine, Université Libre de Bruxelles (Belgique)

INTRODUCTION

L'objet des présentes recherches a été de déterminer dans quelle mesure la chromatographie sur échangeur d'ions (MOORE ET STEIN[1]) est applicable à l'étude de la composition des aliments en acides aminés. Les méthodes chromatographiques décrites ci-dessous se sont montrées appropriées à l'analyse d'un aliment comme la farine de manioc exceptionnellement riche en hydrates de carbone. La démonstration en est donnée dans un autre mémoire présenté de CLOSE *et al.*[2] Ces méthodes ont été utilisées pour le dosage des acides aminés du lait humain entier par SOUPART *et al.*[3], et pour l'analyse d'aliments importants en nutrition animale (orge, foin et tourteau de lin) par DUSTIN *et al.*[4] Au cours de ces études, les considérations fondamentales suivantes de l'analyse alimentaire ont guidé le choix des méthodes:

Le dosage de la totalité des acides aminés d'un aliment. Pour autant que les méthodes le permettent, il est indiqué en matière de nutrition de connaître aussi bien l'apport total en acides aminés (*cf.* ALLISON[5], BIGWOOD[6]) que celui des 10 ou 12 qui se sont avérés les plus essentiels. Lors de dosages chimiques ou microbiologiques, une analyse séparée est nécessaire pour la détermination de chacun des acides aminés. L'intérêt recherché dans la méthode chromatographique réside partiellement dans le fait qu'un chromatogramme unique capable de fournir des résultats pour une dizaine d'acides aminés est susceptible d'en fournir aussi pour la plupart des autres acides aminés, au cours d'une même expérience. La chroma-

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** Professeur titulaire de la Chaire Francqui 1950-51. Membre du Rockefeller Institute for Medical Research, New York.

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tographie est en outre une méthode générale permettant de déceler la présence aussi bien des constituants que l'expérimentateur présume trouver dans son échantillon, que de ceux qu'il ne recherche pas. Un exemple, rencontré au cours des présentes expériences, est celui de l'ornithine trouvée dans des échantillons de farine de manioc[2]. Voici précisément le cas d'un acide aminé pour lequel l'intention ou l'occasion d'en faire le dosage par des méthodes spécifiques pouvait ne pas se présenter.

Analyse d'aliments totaux. Le but étant d'établir un relevé quantitatif complet des acides aminés, il est manifestement préférable d'effectuer une analyse sur l'aliment entier plutôt que de tenter une évaluation de l'apport alimentaire à partir de l'analyse d'extraits protéiques. En effet, tout processus d'extraction comporte en soi la possibilité de perdre certains constituants de l'aliment, contenant des acides aminés. Pour qu'une méthode chromatographique puisse être utilisée de manière sûre pour l'analyse directe d'aliments, il est nécessaire de s'assurer d'abord que la présence de grandes quantités d'hydrates de carbone dans le matériel à hydrolyser n'est pas gênante. Le second article de la présente série[7] démontre que des hydrolysats préparés en présence d'hydrates de carbone peuvent être placés directement sur des colonnes d'échangeur d'ions sans que le dosage des acides aminés n'en soit influencé. Les résultats établissent, d'autre part, la stabilité de la plupart des acides aminés au cours du traitement hydrolytique qu'on leur fait subir en présence d'hydrates de carbone, dans les conditions de dilution adoptées en vue précisément de réduire la formation d'humines au minimum.

Le problème de la destruction de la cystine et du tryptophane ainsi que l'oxydation de la méthionine, lors de l'analyse d'aliments totaux, sont discutés dans le présent article.

La partie expérimentale ci-dessous traite des détails de la méthode utilisée. La chromatographie est effectuée sur des colonnes de Dowex-50- × 12, de 0.9 × 100 cm pour la détermination des acides aminés neutres et acides, et de 0.9 × 15 cm pour celle des acides aminés basiques et de NH_3. La description de la technique chromatographique donnée ci-dessous est limitée aux points pour lesquels l'équipement ou la méthode de MOORE ET STEIN[1] ont été modifiés ou étendus, soit pour faire face aux besoins de l'analyse alimentaire, ou bien encore pour faciliter l'exécution des expériences dans notre laboratoire.

APPAREILLAGE

Fractionneuses. Les analyses furent effectuées à l'aide de quatre types de fractionneuses: un modèle commercial (Technicon Co., New York), basé sur le comptage photoélectrique de gouttes[8], une machine photoélectrique conçue et construite dans notre laboratoire par DUSTIN[9], et deux autres types d'instruments

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conçus respectivement par SCHRAM[10] et par DUSTIN[11], comportant un siphon de 1 ml commandant électroniquement l'avance d'un plateau rotatif. Au cours de nos expériences, les instruments à compteur de gouttes ont répondu aux besoins les plus variés, les modèles à siphon se sont, de leur côté, avérés pleinement satisfaisants pour des fractions de 1 ml et davantage. L'analyse de l'effluent a donné des courbes identiques pour les deux types d'appareil.

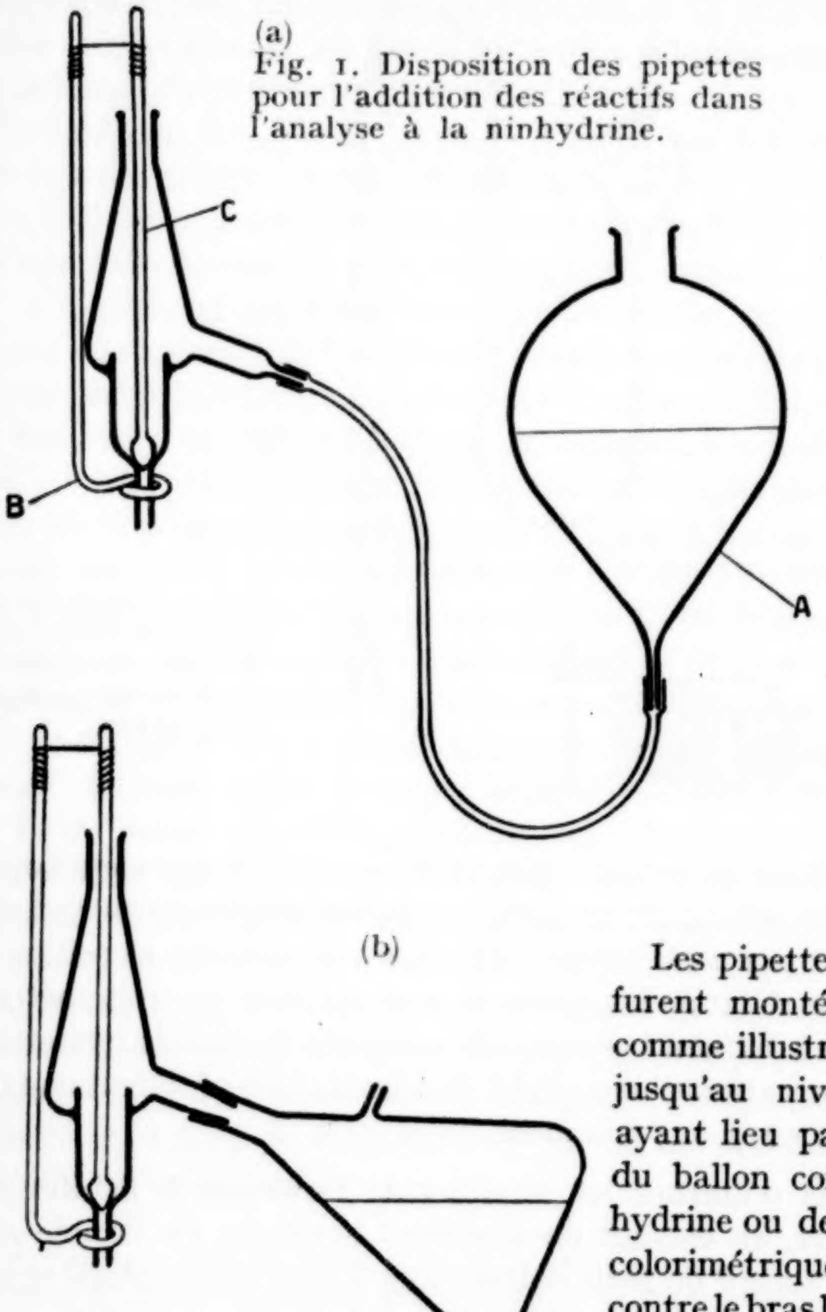

Fig. 1. Disposition des pipettes pour l'addition des réactifs dans l'analyse à la ninhydrine.

Colonnes chromatographiques. Les joints en verre rôdé ont été éliminés et la plaque en verre fritté soudée directement à la partie inférieure de la colonne. La portion de colonne inférieure à la plaque en verre fritté doit avoir un diamètre intérieur d'au moins 5 millimètres.

Pipettes. N'ayant pu disposer de pipettes automatiques actionnées électriquement[12], nous avons essayé divers types de pipettes semi-automatiques à main; les meilleurs résultats furent obtenus au moyen du modèle représenté par la Fig. 1*.

Les pipettes (1 ml et 5 ml de capacité) furent montées dans une position fixe, comme illustré à la Fig. 1*a*, le remplissage jusqu'au niveau du réservoir intérieur ayant lieu par élévation et abaissement du ballon contenant la solution de ninhydrine ou de diluant. Chacun des tubes colorimétriques est rempli en l'appuyant contre le bras latéral (B) de la valve en verre rôdé. En opérant d'une autre manière — qui nous paraît toutefois moins sûre, tant au point de vue de la constance du volume prélevé, que du risque de bris de la pipette — le ballon peut être fixé à un niveau inférieur à celui des tubes rangés dans leur support et la pipette est amenée à la main au niveau de chacun de ces tubes. La même technique peut être suivie au cas où le réservoir à réactif est solidaire de la pipette (Fig. 1*b*). Toutes les connections sont réalisées au moyen de tuyau en matière plastique (Tygon ou polyéthylène) ou de joints rôdés, étant donné que les solvants alcooliques utilisés dans la méthode à la ninhydrine ne peuvent pas venir au contact de caoutchouc. Les valves en verre peuvent nécessiter un rodage supplémentaire au moyen de fin émeri lorsqu'elles ne sont pas parfaitement étanches aux solvants alcooliques.

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* Mesureur ,,Blitz'' à renversement (J. E. Gerber & Co., Zürich, Suisse). Voir aussi ,,Traité pratique des essais du lait'' par Schneider-Gerber, 1946. Éditeur C. J. Wyss. S. A. à Berne.

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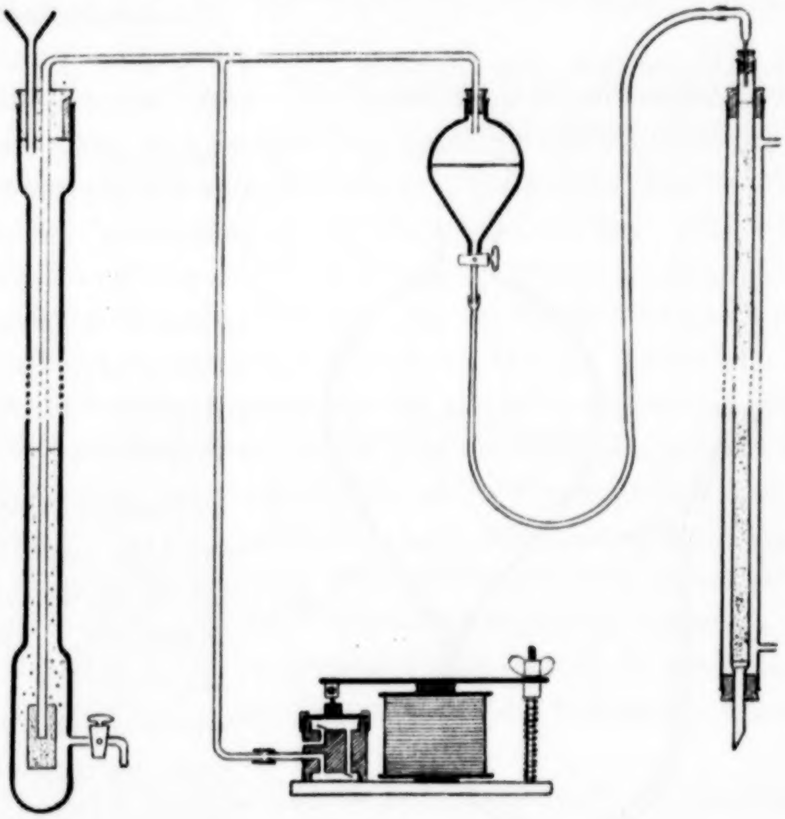

Fig. 2. Application d'une pression d'air sur les colonnes à l'aide d'une pompe d'aquarium.

La constance de volume du débit de la pipette de 1 ml, vérifiée par gravimétrie, est de 1%. Un retrait brusqué du tube à essai ou de la pipette favorise la fermeture de la valve et prévient la formation d'une goutte pendante. Une cinquantaine de tubes peuvent être remplis en 3 à 4 minutes.

Pression d'air. Il est aisé d'amener les colonnes de Dowex-50 à débiter au rythme désiré de 4 ml/heure, en élevant ou abaissant le niveau du liquide au-dessus de l'adsorbant. Un raccord de petit diamètre en Tygon est intercalé entre le sommet de la colonne et l'ampoule contenant le tampon (Fig. 2) de sorte que celle-ci peut être amenée à la hauteur voulue. Quand la pression ainsi obtenue n'est pas suffisante, une pression d'air complémentaire est appliquée au moyen d'une pompe d'aquarium débitant au travers d'un disque poreux à la base d'une colonne d'eau de 200 cm de hauteur; la pression d'air peut être modifiée en faisant varier le niveau d'eau (Fig. 2).

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MODE OPÉRATOIRE

Hydrolyse. Un échantillon de l'aliment, correspondant à environ 8 mg d'azote (env. 50 mg de protéine) est chauffé à reflux pendant 24 heures dans 200 ml de HCl 6*N*. Dans ce but, il est fait usage d'un bain d'huile à chauffage électrique, maintenu à 135-140° par un régulateur thermostatique. Les conditions de dilution appliquées pour l'hydrolyse (plus de 100 ml de HCl 6*N* par g d'aliment) trouvent leur origine dans le fait que la formation d'humines est moindre en solution diluée (JACOBSEN[13], STEIN ET MOORE[14]). Ce rapport élevé entre la quantité d'acide et l'échantillon fut adopté au cours d'essais sur des aliments contenant 98% d'hydrates de carbone, et fut utilisé tout au long de nos présentes études. La quantité de HCl est vraisemblablement plus importante qu'il n'est nécessaire dans le cas d'aliments de teneur plus élevée en protéines.

L'hydrolysat est filtré sur verre fritté afin de séparer les humines; le filtrat ainsi que les eaux de lavage sont ensuite concentrés à sec dans un évaporateur du type décrit par CRAIG, CREGORY ET HAUSMANN[15]. Le stade final de l'évaporation a lieu dans un ballon de 50 ml de capacité. Le résidu est dissous dans 3 ml de HCl 0.5*N* qui sont transférés quantitativement dans un ballon jaugé de 10 ml par lavages successifs au moyen de HCl 0.5*N*. La petite quantité de matière insoluble obtenue à ce stade est éliminée par centrifugation; la solution surnageante est conservée à la glacière dans un flacon à bouchon rodé, en attendant la chromatographie. Si le dosage de l'azote humique s'impose, le culot de centrifugation est lavé et joint au résidu insoluble obtenu précédemment; l'azote y est dosé par micro-Kjeldahl. Tout l'azote humique n'atteint fréquemment pas 1% de l'azote total; souvent même il ne s'y trouve qu'à l'état de trace indosable.

Etant donné que l'NH_3 contenu dans l'hydrolysat va être dosé par chromatographie, il est nécessaire d'effectuer une hydrolyse de contrôle au moyen de 200 ml de HCl prélevé sur le même lot que celui utilisé pour les expériences. L'essai à blanc comporte toutes les étapes citées plus haut. Une aliquote de 1 ml prélevée sur les 10 ml de la solution finale est amenée à pH 5 environ au moyen de soude 0.5*N* et sa teneur en NH_3 est mesurée par la méthode à la ninhydrine en faisant usage de 2 ml de réactif. Dans nos conditions opératoires, la correction ne s'éleva qu'à 5 μg de NH_3 environ par ml de la solution portée sur les colonnes chromatographiques*.

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* En pratique, il est avantageux de préparer une solution-stock de HCl 6*N*, conservée dans un flacon avec bouchon en verre ou matière plastique et protégée contre les contaminations par l'NH_3. Le résultat de l'analyse à blanc obtenu pour l'NH_3 sur chacun des lots peut servir pour de multiples hydrolyses. Il est essentiel que les réfrigérants utilisés pour l'hydrolyse à reflux soient rincés soigneusement à l'eau après chaque usage afin d'éviter les contaminations par le chlorure d'ammonium qui pourrait s'y être déposé. Durant l'hydrolyse, le sommet des réfrigérants est enrobé de papier filtre afin d'intercepter l' NH_3 de l'air. Le HCl 0.5*N* utilisé pour dissoudre l'hydrolysat doit être préparé fraîchement à partir de la solution-stock de HCl.

Chromatographie. Il est important que l'ajustement du pH de l'échantillon soit réalisé avec soin étant donné que l'addition d'échantillons d'un pH supérieur à celui de la colonne entraînera un étalement des pics dans le diagramme du liquide effluent. Une titration préliminaire est effectuée afin de règler la neutralisation nécessaire en vue d'amener l'hydrolysat au pH approprié, au moment où il va être porté sur la colonne de Dowex-50. A 1 ml d'hydrolysat on ajoute 1 ml de tampon 0.2*M* de pH 5, puis goutte à goutte de l'hydroxyde de sodium *N* contenu dans une burette, jusqu'à ce que le pH soit de 2.5 (pour la colonne de 100 cm) ou de 4.0 (pour la colonne de 15 cm), les mesures étant effectuées à l'électrode de verre ou au papier indicateur sensible à 0.2 unité en pH.

Pour l'analyse chromatographique on utilise de préférence une autre aliquote de 1 ml de l'hydrolysat. On ajoute 1 ml de tampon de pH 5 et le nombre de gouttes de NaOH nécessaire. La totalité de l'échantillon est transférée quantitativement du tube sur la colonne de Dowex-50 en effectuant 3 rinçages de 0.3 ml au moyen de tampon de pH 2.5* ou 4.2**.

Les chromatogrammes sur colonne de 100 cm sont interrompus après l'émergence de la tyrosine et de la phénylalanine***, après quoi la colonne est lavée à la soude 0.2*N* (100 ml) en vue de sa réutilisation. Les colonnes sont thermostatisées au moyen d'un manchon à circulation d'eau dont la température est ajustée successivement à 37.5°, 51° et 75° au moyen de bains-marie à pompes centrifuges****. Les colonnes de 15 cm furent utilisées à la température du laboratoire; une légère élévation du pH du second tampon à 6.85 au lieu de pH 6.78 s'est avérée désirable afin d'assurer la séparation complète de l'histidine et de la lysine, dans les conditions de température règnant en moyenne dans notre laboratoire (c'est-à-dire 20° C (± 3°)); par temps chaud en juillet, cette température moyenne tend exceptionnellement à s'élever et la position des pics aux diagrammes des colonnes de 15 cm est temporairement influencée de ce fait. A 20° la position des pics tend à être déplacée vers la droite sur les diagrammes, par rapport à ce qui se passe à 25°.

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* La solution-tampon de pH 2.5 est préparée en mélangeant 75 volumes de tampon 0.2*M* de pH 5, 25 volumes de HCl *N* et 50 volumes de H_2O.

** La solution-tampon de pH 4.2 est préparée en mélangeant 50 volumes de tampon 0.2*M* de pH 5, cinq volumes de HCl *N* et 45 volumes de H_2O.

*** Les chromatogrammes sur colonne de 100 cm furent généralement commencés le lundi et terminés le vendredi après l'apparition de la tyrosine et de la phénylalanine. Les chromatogrammes sur colonne de 15 cm requièrent 2 jours.

**** La température de l'eau ne peut pas tomber de plus de 1° au cours de son transit dans la partie de son circuit située en dehors du bain marie. La température de 51° nous a généralement donné de meilleures séparations qu'à 50°, dans la région des fractions 225 à 300 ml.

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Analyse des fractions effluentes. La concentration du chlorure stanneux dans le réactif à la ninhydrine[12] fut portée de 0.8 g à 1.0 g par litre*. La solution est conservée sous azote dans un premier réservoir[12] communiquant avec un second qui contient de l'eau et est placé à un niveau supérieur de manière à maintenir le réactif sous une légère pression et à provoquer ainsi son écoulement par le tube de sortie qui est muni d'un robinet rôdé. Directement avant l'usage, une portion de 60 ml de réactif (pour 50 tubes environ) est prélevée hors du réservoir et transférée dans l'ampoule attenant à la pipette de 1 ml (Fig. 1a). Un ml de réactif, plutôt que deux, par raison d'économie, est ajouté à chaque fraction de liquide effluent, les tubes sont ensuite mis au bain-marie bouillant pendant 30 minutes. En utilisant 1 ml de la solution de ninhydrine ci-dessus, il a été constaté que le rendement coloré maximum était obtenu en neutralisant les fractions effluentes par l'addition de 0.1 ml des solutions suivantes pour chacun des tampons correspondants: pH 3.4: NaOH $1.25N$; pH 4.25: NaOH $0.75N$; pH 6.8: HCl $0.25N$; pH 6.5: HCl N. Ces solutions furent placées dans des réservoirs équipés d'un siphon se terminant par un ajutage capillaire de 7 mm de diamètre extérieur, délivrant des gouttes de 0.1 ml. La vitesse d'écoulement est réglée à 2 secondes environ par goutte, au moyen d'une pince de Mohr sur tube plastique. La dilution est effectuée par l'addition de 5 ml d'un mélange de volumes égaux d'alcool et d'eau au moyen d'une seconde pipette semi-automatique. Les 20 premiers ml délivrés par la pipette sont écartés afin d'éliminer certains produits insolubles dans l'eau, et que le tube plastique de celle-ci aurait pu céder au mélange au cours de la nuit. Nous avons vérifié au cours de ce travail que l'alcool éthylique, dénaturé à l'éther ou non, peut être substitué à l'alcool *n*-propylique, plus coûteux et plus difficile à obtenir. Les rendements colorés à la ninhydrine furent identiques au cours d'essais au moyen de ces divers diluants.

Les rendements colorés par rapport à la leucine de tous les acides aminés courants furent vérifiés dans les conditions expérimentales décrites ci-dessus, et concordent avec les valeurs publiées[1,12] à l'exception de celui de la proline, pour laquelle le rendement s'est élevé à 0.30 par suite de la plus grande durée de chauffe. La β-alanine constitue un cas spécial, étudié par CROKAERT *et al.*[16].

L'obtention de „*blancs*" satisfaisants lors de l'analyse colorimétrique des tubes provenant des fractionneuses a nécessité l'application des mesures recommandées pour éviter la contamination par l'NH_3. La surface intérieure de toutes les fractionneuses fut recouverte de papier imprégné d'acide citrique. Les bouchons servant à boucher les tubes en attendant l'analyse furent traités aussi par l'acide citrique. De plus, il nous a fallu pallier à une contamination éventuelle par des particules de liège. Dans ce but tous les bouchons furent enrobés dans des feuillets de cellophane imperméable; en utilisant une variété se soudant à chaud, ces feuillets peuvent être amenés à épouser la forme des bouchons par pression sur une plaque chauffante.

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* En principe, cet ajustement aurait dû porter cette concentration de 0.8 à 1.6, puisque le volume de réactif à la ninhydrine employé fut réduit de moitié. L'expérience a démontré toutefois que la concentration du chlorure stanneux de 1 p. mille est suffisante.

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Après traitement à la ninhydrine, on observe quelquefois une coloration jaunâtre dans plusieurs tubes après la 24e fraction de liquide effluent (colonne de 100 cm). Ce phénomène peut se produire pour des fractions dont le pH est trop élevé, la coloration obtenue étant en effet celle qu'on obtient en chauffant le réactif à la ninhydrine à pH 7 ou 8*. La portion d'effluent en question correspond aux quelques ml de solution dans lesquels était contenu l'échantillon; elle émerge après le passage d'une quantité de liquide correspondant au volume de rétention de la colonne, c'est-à-dire après environ 24 ml en cas de colonne de 100 cm. Si le pouvoir tampon de l'échantillon initial est inférieur à celui du tampon de pH 3.4, l'addition de 0.1 ml de NaOH 1.25*N* entraînera un pH trop élevé dans quelques tubes; ceci fera apparaître une coloration jaunâtre dans quelques fractions, qui pourrait en imposer pour un pic dû à un constituant aminé au diagramme d'élution.

Calculs. Une courbe-étalon, basée sur l'analyse d'aliquots de 1 ml prélevés sur des solutions de concentration variable en leucine dans du tampon de pH 4.2, et amenés au pH voulu par addition de 0.1 ml de NaOH 0.75*N*, a servi à l'établissement du tableau de conversion**. Les calculs peuvent être abrégés notablement si ce tableau[12] est établi en micromoles par litre par rapport aux lectures directes (c'est-à-dire celles correspondant à la densité optique), pour les conditions spécifiques dans lesquelles sont analysées les fractions de 1 ml d'effluent additionnées de 0.1 ml de réactif de neutralisation. Les corrections de volume des pipettes de 1 et de 5 ml sont aussi à intégrer dans le tableau. La quantité d'acide aminé représentée par un pic donné, exprimée en micromoles, est égale à la somme des concentrations trouvées pour les différents points de la courbe, divisée par 1000 et par le facteur coloré.

La précision de la présente technique chromatographique telle qu'elle fut adoptée dans notre laboratoire, c'est-à-dire en faisant usage de 1 ml de réactif à la ninhydrine, fut vérifiée au moyen du même mélange synthétique d'acides aminés purifiés que celui utilisé pour la standardisation de la méthode initiale[1]. Pour des chromatogrammes uniques, la récupération de chacun des constituants s'éleva à 100 ± 5%. Lors d'expériences effectuées en double, la moyenne des résultats nous a presque toujours fourni des résultats s'écartant de moins de 3% de la théorie.

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* Cette coloration tend à virer à l'orangé si le pH est supérieur à 8.

**Dans les présentes expériences, les tubes calibrés pour photométrie furent divisés en 3 groupes, le diamètre intérieur des tubes appartenant à chacun des groupes concordant entre eux à moins de 1% près. La courbe-étalon fut établie au moyen des tubes appartenant au groupe le plus nombreux tandis que les résultats obtenus au moyen des autres séries étaient corrigés par un facteur approprié (0.984; 0.967).

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Quant aux valeurs qui ont servi à dresser les diagrammes figurant dans la littérature, elles correspondent à celles du tableau qui expriment des ,,*équivalents leucine*", c'est-à-dire celles qui n'ont *pas* été corrigées pour les coefficients colorés spécifiques de chaque acide aminé, sauf pour la proline (rendement coloré 0.30) afin de rendre la dimension de ce pic approximativement comparable à celle des autres acides aminés.

Identification des pics. Les 18 ou 20 acides aminés les plus communs sont généralement les seuls décelables dans les protéines alimentaires. Aussi croyons-nous qu'en analyse alimentaire les résultats de la chromatographie peuvent être interprêtés avec une sécurité suffisante, en fonction de l'emplacement de ces divers acides aminés sur Dowex-50. Pour des mélanges susceptibles de contenir divers acides aminés plus rares, l'effluent correspondant à un pic donné peut être dessalé (DRÈZE *et al.*[17]) de manière à ce que son identification puisse être poursuivie par chromatographie sur papier, comme cela a notamment été pratiqué par STEIN[18] dans ses expériences sur les acides aminés de l'urine.

DISCUSSION

Si les chromatogrammes sont capables de fournir des données quantitatives pour tous les acides aminés d'un hydrolysat, il n'en subsiste pas moins la difficulté créée par l'instabilité de certains d'entre eux aux conditions d'hydrolyse. L'étude des aliments soulève en effet les problèmes particuliers suivants:

Cystine. La cystine et la cystéine sont connues pour leur instabilité au cours de l'hydrolyse en présence d'hydrates de carbone. La chromatographie d'hydrolysats d'aliments sur Dowex-50 ne fournit généralement pas de pic décelable ou mesurable de cystine. Une solution possible à ce problème consiste à oxyder la cystine et la cystéine à l'état d'acide cystéique dans l'aliment intact, avant l'hydrolyse, un acide aminé étant ainsi obtenu qui résiste parfaitement à l'hydrolyse par HCl. Ce moyen a conduit à l'élaboration d'une méthode chromatographique satisfaisante pour le dosage de la cystine sous forme d'acide cystéique (SCHRAM *et al.*[19]), technique qui fut utilisée pour l'obtention des données reprises dans les présents travaux.

Méthionine. Ce fut tout d'abord au cours de nos expériences chromatographiques sur Dowex-50 que nous avons faites en collaboration avec J. CLOSE ET E. L. ADRIAENS en analysant la farine de manioc[2], qu'il apparut le fait que le pic de la méthionine peut aisément s'effacer tout en faisant apparaître un pic nouveau occupant la place du sulfoxyde correspondant, au cours de l'hydrolyse usuelle

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par HCl. Dans un hydrolysat d'aliment, une portion variable de la méthionine peut apparaître sous la forme de son sulfoxyde. Cette tendance constitue une difficulté fondamentale pour le dosage précis de la méthionine dans les hydrolysats acides aussi bien de protéines pures que d'aliments. L'étude de cette question fut reprise plus spécialement par l'un de nous (E. SCHRAM) dans une étude systématique qu'il fit en soumettant des solutions de méthionine à l'action de l'hydrolyse acide par HCl. En présence d'amidon, il ne se forme pratiquement que du sulfoxyde et éventuellement une trace seulement de sulfone*. Une évaluation approximative de la teneur en méthionine à partir des diagrammes peut être provisoirement adoptée sur la base des observations consignées au Tableau I. Le sulfoxyde émerge sous forme d'un pic en tête et complètement séparé de l'acide aspartique sur colonne de 100 cm. Son rendement coloré vaut 1.02.

TABLEAU I

RENDEMENTS EN MÉTHIONINE ET SULFOXYDE DE MÉTHIONINE AU COURS D'EXPÉRIENCES SUR L'HYDROLYSE

Six milligrammes de méthionine sont traités par HCl 6*N* bouillant en présence d'amidon

Quantité de HCl (24 h à reflux) ml	Quantité d'amidon ajoutée g	% de 6 mg de méthionine récupérée sous forme de		Correction empirique: 20% de la quantité de sulfoxyde	% total récupéré y compris la correction empirique
		méthionine	sulfoxyde de méthionine		
20	1,0	65	28	6	99
200	1,0	50	41	8	99
200	1,0	46	44	9	99
10	0,1	80	20	4	104

En appliquant une correction empirique de 20% à la quantité de sulfoxyde trouvée, la quantité totale de méthionine ainsi obtenue est sensiblement reproductible (Tableau I). La sulfone apparaît à hauteur du pic de la thréonine; elle ne fut cependant jamais rencontrée qu'à l'état de traces lorsque l'hydrolyse s'opère en présence d'hydrates de carbone ($< 2\%$).

Le calcul ci-dessus ne constitue cependant pas une solution finale du problème du dosage chromatographique de la méthionine; celui-ci nécessite peut-être de plus amples recherches sur la préparation d'hydrolysats en présence de réducteurs ou sur une technique permettant l'oxydation complète de la méthionine avant chromatographie. Pour diverses substances analysées par la méthode actuelle, il nous a été loisible, en ce qui concerne la méthionine, de compléter les données de la chromatographie par les résultats de dosages microbiologiques, grâce à l'aimable coopération du Professeur J. H. BOUCKART et ses collaborateurs de l'Université de Gand.

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* Cette étude sera plus longuement développée dans une thèse de doctorat ès sciences que E. SCHRAM compte défendre à la Faculté des Sciences de l'Université de Bruxelles. Nous en avons tiré certaines données réunies dans le Tableau I.

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Tryptophane. La chromatographie des produits formés lors de l'hydrolyse alcaline du tryptophane n'a été étudiée que succinctement, de sorte qu'une méthode satisfaisante pour le dosage du tryptophane dans les aliments n'a pas pu être mise au point. Nos analyses n'ont donc pas pû englober cet important acide aminé, et nous avons recours aussi à la méthode microbiologique pour le dosage du tryptophane dans les aliments soumis à notre étude.

Sérine et thréonine. Les résultats concernant l'analyse de substances alimentaires n'ont pas été corrigés pour la perte éventuelle de petites quantités d'acides aminés hydroxylés. REES[20] a démontré, au cours d'expériences minutieuses, que la sérine peut être décomposée à raison de 10%, la thréonine à raison de 5%, après 24 heures d'hydrolyse acide. Il ne nous a pas été possible d'établir avec exactitude le degré de destruction de ces acides aminés dans nos conditions d'hydrolyse. Un prochain article[7] traite avec plus de détails de cette question et indique que les pertes enregistrées n'excèdent pas celles observées par REES. Il nous a semblé aussi que dans le cas d'aliments il n'était vraisemblablement pas indispensable de tenter la correction des résultats pour la sérine et la thréonine.

Ammoniaque. Lors du dosage chromatographique de l'NH_3 total dans un hydrolysat, il y a lieu de considérer en particulier la correction mentionnée antérieurement, due à l'NH_3 présent dans l'HCl, ainsi que l'intégration adéquate du pic de l'NH_3 sur les diagrammes obtenus au moyen des colonnes de 15 cm. Pour les raisons exposées ailleurs[1], le „*blanc*" pour l'NH_3 doit être choisi après le pic plutôt que devant lui. La mobilisation de l'NH_3 contenu dans les tampons entraîne notamment la formation d'un plateau dans les valeurs trouvées à la ninhydrine, dont il ne peut pas être tenu compte lors de l'intégration. L'NH_3, provenant de l'échantillon, fournit un pic ramassé se superposant à la ligne de base surélevée.

Hydrates de carbone. L'hydrolyse opérée en présence des hydrates de carbone des aliments donne lieu à la formation de produits qui migrent en tête de l'acide aspartique sur colonne de 100 cm et donnent lieu, après analyse à la ninhydrine, à un pic rouge important vers le 40me ml de liquide effluent. Ce pic s'est présenté jusqu'à présent dans les hydrolysats de tous les produits contenant les hydrates de carbone et que nous avons soumis „*in toto*" au traitement hydrolytique acide. Ce fut le cas de nos analyses du lait (SOUPART *et al.*[3]), de la farine de manioc (CLOSE *et al.*[2]), de l'orge, du foin et du tourteau de lin (DUSTIN *et al.*[4]). Depuis lors il fut retrouvé aussi dans d'autres milieux naturels. Ce pic rouge fut donc rencontré lors de l'hydrolyse de matériaux contenant notamment de l'amidon, de la cellulose, du glucose ou du lactose. Il a pu être établi que le glucose ne donne pas directement cette réaction tandis que l'acide lévulinique par exemple, se comporte exactement comme les produits trouvés dans l'hydrolysat. Les substances responsables de ce pic rouge ne paraissent pas contenir de l'azote; en effet, leur position dans le chromatogramme et leur maximum d'absorption (520 mμ) sont les mêmes pour les pics obtenus à partir d'hydrolysats d'aliments et pour ceux obtenus en soumettant au traitement hydrolytique acide une solution pure de glucose ou bien encore une solution d'amidon lavé exempt d'azote titrable, et en absence d'acides aminés dans les deux cas. La capacité des colonnes de Dowex-50 est telle que des quantités importantes de produits de dégradation des hydrates de carbone n'interfèrent pas dans le dosage des acides aminés.

Expression des résultats. Dans la présente série d'expériences, les résultats d'analyse ont été exprimés de la façon suivante:

a) en mg de chacun des acides aminés par 100 g d'aliment, l'humidité et la teneur en N de ce dernier étant connues.

b) en % N pour chacun des acides aminés par rapport à l'N total de l'aliment.

Les résultats n'ont pas été recalculés par rapport à une valeur arbitraire de 16 g d'N[21]. L'apport diététique peut être évalué très aisément à partir du nombre de mg d'acide aminé par g d'aliment, corrigé, si nécessaire, pour des différences dans la teneur en azote des échantillons. Les quantités relatives d'acides aminés dans les protéines alimentaires peuvent être comparées par tabulation des pourcentages d'N par rapport à l'N total. La composition d'un mélange bien équilibré en acides aminés (lait humain ou autre étalon) et exprimé de la même façon, peut servir de guide dans les comparaisons.

CONCLUSIONS

La chromatographie sur échangeur d'ions convient à l'analyse quantitative quasi-complète en acides aminés des aliments. Le temps requis pour une analyse doit être retenu dans les appréciations sur l'applicabilité générale de la méthode. Plus d'une semaine est nécessaire pour l'étude d'un échantillon alimentaire. La présente technique peut être considérée comme un apport aux instruments fondamentaux permettant d'étudier la composition des aliments, tandis que dans le domaine des acides aminés, il est précieux d'avoir différentes méthodes à sa disposition.

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RÉSUMÉ

Une technique détaillée est décrite pour la détermination de la composition des aliments en acides aminés par chromatographie de l'hydrolysat sur colonne de Dowex-50 selon la méthode de MOORE ET STEIN. Pratiquement tous les acides aminés courants peuvent être dosés. Le dosage de la méthionine est toutefois compliqué par l'oxydation partielle de cet acide aminé en sulfoxyde au cours de l'hydrolyse. Une méthode chromatographique satisfaisante pour le tryptophane n'a pas encore pu être mise au point. Il est fait mention du développement auxiliaire d'une méthode chromatographique pour le dosage de la cystine (en présence d'hydrates de carbone) à l'état d'acide cystéique et de l'utilisation de ces techniques combinées pour l'analyse de divers aliments importants en nutrition humaine et animale.

SUMMARY

A detailed procedure is presented for the determination of the amino acid composition of foods by chromatography of the hydrolysates on columns of Dowex-50 by the method of MOORE AND STEIN. Nearly all of the common amino acids can be determined. The measurement of methionine, however, is complicated by partial oxidation of the amino acid to the sulfoxide during acid hydrolysis. A satisfactory chromatographic method for tryptophan has not been obtained as yet. Cross-reference is given to the auxiliary development of a chromatographic method for the determination of cystine (in the presence of carbohydrate) as cysteic acid and to the utilization of these combined techniques in the analysis of several foods of importance in human and animal nutrition.

ZUSAMMENFASSUNG

Es wird eine eingehende Methode zur Bestimmung der Zusammensetzung der Aminosäuren in Lebensmitteln durch die chromatographische Untersuchung des Hydrolysats mit der Dowex-50-Säule nach der Methode von MOORE AND STEIN beschrieben. Praktisch alle gangbaren Aminosäuren können bestimmt werden. Die Bestimmung des Methionins wird jedoch durch die teilweise Oxydation dieser Aminosäure zum Sulfoxyd im Laufe der Hydrolyse erschwert. Eine befriedigende chromatographische Methode für Tryptophan konnte noch nicht aufgestellt werden. Es wurde die Entwicklung einer chromatographischen Hilfsmethode zur Bestimmung von Cystin in Gegenwart von Kohlenhydraten als Cysteinsäure und die Benützung dieser kombinierten Methoden zur Analyse von verschiedenen für die menschliche und tierische Ernährung wichtigen Lebensmitteln erwähnt.

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A PRECISE HETEROMETRIC MICRO-DETERMINATION OF LEAD OR CITRIC ACID

by

M. BOBTELSKY AND B. GRAUS

Department of Inorganic and Analytical Chemistry of the Hebrew University, Jerusalem (Israël)

A heterometric method (= photometric titration of suspensions), developed by the first author with co-workers, was used for the study of the composition and structure of the complexes formed between lead and citrate.

In this paper we present the analytical application of lead citrate for the micro-determination of lead or citrate. Both may be determined by a single titration which takes from 10 to 15 minutes. The analyzed solution contains approximately 0.1—1.0 mg of lead or citric acid per one ml. The error, using a 50% alcoholic medium, lies between zero and 1%. Many available photometers may be adapted for such heterometric titrations. (A specially designed "Heterometer" may be supplied if desired).

EXPERIMENTAL

A "heterometer" (= a photometer adapted for the study of suspensions) was used[1]. In all experiments the height of the initial layer of the analysed solution was about 1 cm (exception, exp. 10). The cylindrical vessel had a diameter of ∾ 3.6 cm. The light passed vertically through the solution to the selenium cell, which was connected to a sensitive microampermeter (1 microamp = 16 cm). The solution was stirred vigorously during the titration. A precision microburet (divided into 0.01 cm) was used. All experiments were carried out at room temperature (18—25° C). The chemicals used were C.P. Baker's.

RESULTS

Table I and Figs. 1—3 represent a small fraction of the titrations made. Experiments repeated at different times and at different room temperatures give similar results, although the optical density values for the maxima differed somewhat. The composition of the experiments presented in Figs. 1—3 and the results are compiled (under the same numbers) in Table I. Fig. 1 presents the

TABLE I

Experiment number	Composition	X Calcul. ml	X found ml	mg Lead present	mg Lead found	error mg	error %	Maxim. optical density
1	2 ml 0.005*M* $Pb(NO_3)_2$ + 8 ml H_2O + X ml 0.005*M* Na_3Ci.aq	1.33	1.29	2.072	2.010	—0.062	—3.0	0.23
2	3 ,, 0.005 ,, ,, + 7 ,, ,, + X ,, 0.005 ,, ,, ,,	2.00	1.93	3.108	2.999	—0.109	—3.5	0.29
3	5 ,, 0.005 ,, ,, + 5 ,, ,, + X ,, 0.005 ,, ,, ,,	3.33	3.23	5.180	5.025	—0.155	—3.0	0.47
4	6 ,, 0.005 ,, ,, + 4 ,, ,, + X ,, 0.005 ,, ,, ,,	4.00	3.88	6.216	6.030	—0.186	—3.0	0.52
5	10 ,, 0.01 ,, ,, + X ,, 0.02 ,, ,, ,,	3.33	3.30	20.721	20.535	—0.186	—1.0	1.01
6	5 ,, 0.005 ,, ,, + 5 ml alc. + X ml 0.005*M* Na_3Ci.50% alc.	3.33	3.30	5.180	5.13	—0.05	—0.9	0.08
7	5 ,, 0.01 ,, ,, + 5 ,, ,, + X ,, 0.01 ,, ,, 50% ,,	3.33	3.30	10.360	10.267	—0.093	—0.9	0.17
8	3.75 ,, 0.02 ,, ,, + 1.25 ml H_2O + 5 ml alc. + X ,, 0.02 ,, ,, 50% ,,	2.50	2.50	15.54	15.54	0.0	0.0	0.25
9	5 ,, 0.02 ,, ,, + 5 ml alc. + X ,, 0.02 ,, ,, 50% ,,	3.33	3.35	20.721	20.845	+0.124	+0.6	0.35
10	5 ,, 0.01 ,, ,, + 5 ,, H_2O + 10 ml alc. + X ,, 0.01 ,, ,, 50% ,,	3.33	3.30	10.360	10.267	—0.093	—0.9	0.17
11	4 ,, 0.005 ,, Na_3Ci+6 ml H_2O+ X ml 0.01*M* $Pb(NO_3)_2$ Max. opt. density:	3.00	3.02				+0.7	0.53
	Point of initial precipit.:	2.00	1.97			—1.5	—	
12	6 ,, 0.005 ,, ,, + 4 ,, ,, + X ,, 0.01*M* ,, Max. opt. density:	4.50	4.50			0.0	0.66	
	Point of initial precipity.:	3.00	2.95			—1.7	—	

results of titrations of dilute water solutions of lead nitrate with sodium citrate (direct titrations). Fig. 2 presents results of similar titrations in a 50% alcoholic medium. Fig. 3 shows results of reverse titrations in water solution. The results are as follows:

Titrations in water solutions

Direct titrations. As Table I shows, the results are not of the highest accuracy. If we compare experiments 1—5 (Table I) we see that the optical density values of the maxima are almost proportional to the amount of lead (or citrate) in solution. As Fig. 1 shows, the *first maximum point* obtained gives in all cases

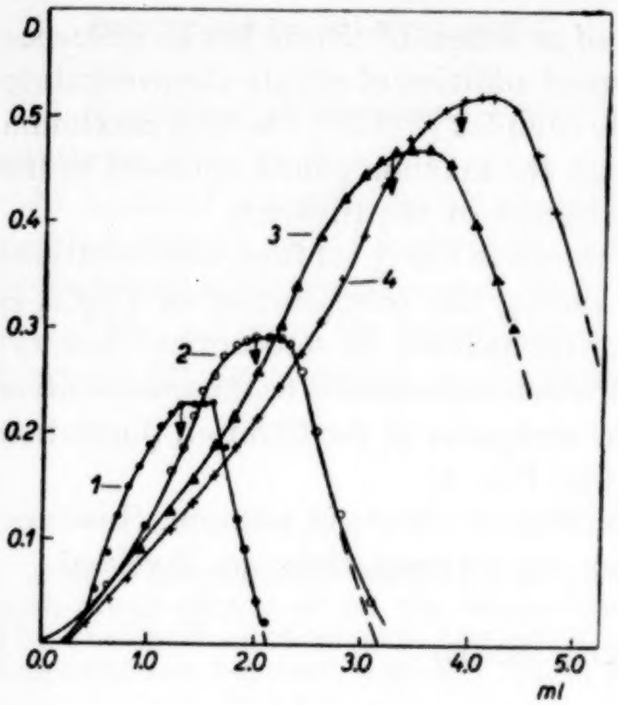

Fig. 1. Titrations of lead nitrate with sodium citrate in water solutions.

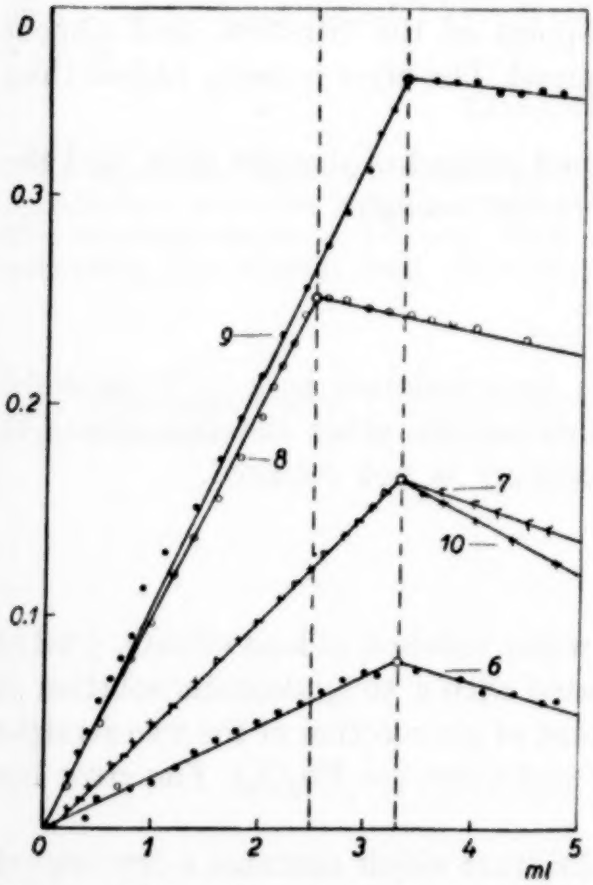

Fig. 2. Titrations of lead nitrate with sodium citrate in 50% alcoholic solutions.

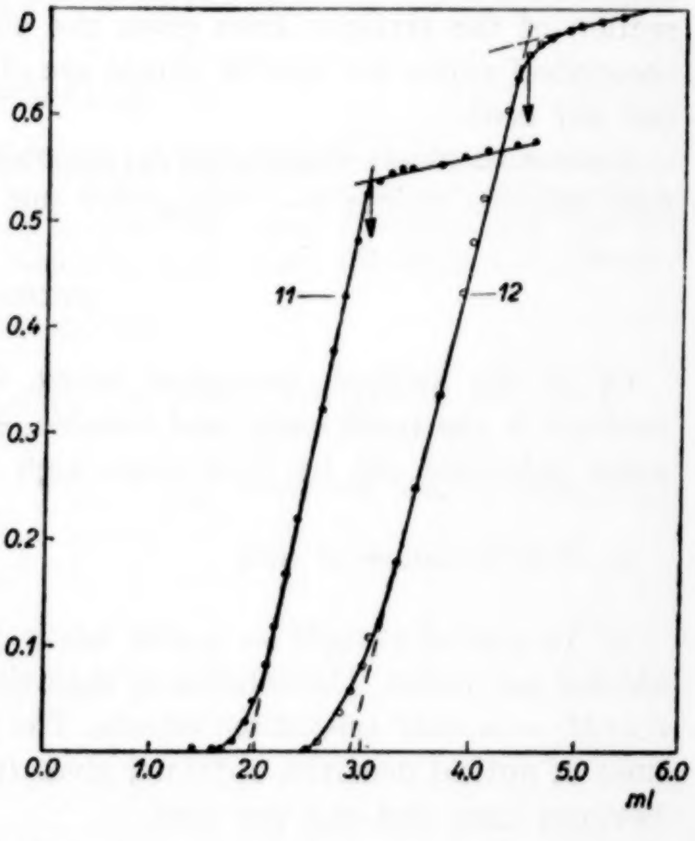

Fig. 3. Titrations of sodium citrate with lead nitrate in water solutions.

the end-point of the titration. The addition of an excess of citrate has no influence at first on the optical density, but on continued addition of citrate the precipitate begins to dissolve by formation of the soluble complex $[PbCi]^-$. The first maximum point can be found by drawing a line through the maxima points obtained in the curve. The first point of contact is the end-point of the titration.

Reverse titrations. Two such titrations are shown in Fig. 3. At first, clear solutions are obtained. The rise in optical density during the precipitation of Pb_3Ci_2 is steep and linear. If the curve obtained is extrapolated to zero optical density, the *initial point* of precipitation is obtained which corresponds to the quantitative formation of a soluble complex $[PbCi]^-$. The end-point of the titration (formation of Pb_3Ci_2) is obtained by extrapolation (see Fig. 3).

Both points may be used for the determination of citrate in solution. However, the results of Fig. 2 are more reliable since no extrapolations are involved.

Titrations in 50% alcohol

Direct titrations. Curves 6—10 (Fig. 2) and Table I give the results of titrations of lead solutions with citrate. The optical density values for the maxima are much lower (almost 1/4) than in water solutions. By using an absorption layer of approximately 2 cm (curve 10), higher density values may be obtained. The intersection of the straight lines gives the end-point of the titration, and almost theoretical values for lead or citrate are obtained. The error is never higher than one per cent.

Reverse titrations. Convex curves are obtained instead of straight lines, and the first maxima points (= Pb_3Ci_2) are not reliable enough.

METHODS

Of all the methods presented below, the determination in a 50% alcoholic medium is the most exact and reliable. However, the other determinations in water solutions can be used when high accuracy is not required.

1. Determination of lead

a) To 5 ml of $0.005M$ — $0.02M$ neutral water solution of lead nitrate, 5 ml of alcohol are added. The solution is then titrated with a 50% alcoholic solution of $0.01M$ — $0.02M$ tri-sodium citrate. The point of intersection of the two straight lines of optical densities obtained gives the end-point (= Pb_3Ci_2). The error lies between zero and one per cent.

b) 10 ml of a neutral water solution of lead nitrate which contains a few mg of lead are titrated with an $0.005M$ solution of trisodium citrate. The first optical density maximum point obtained gives the end-point (= Pb_3Ci_2). The error is $\sim$ 0.1 mg.

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2. *Determination of citric acid*

a) A solution of known concentration of lead nitrate is titrated with sodium citrate exactly as in 1 a.

b) 10 ml of a neutral water solution which contains a few mg of citric acid is titrated with an $0.01M$ lead nitrate solution. A straight line is drawn through the optical density points obtained. Both the point of intersection with the abscissa (= 1 Pb : 1 Ci) or the extrapolated optical density points of the maximum (3 Pb : 2 Ci) may be used for the determination. The error is ∾ 1 — 2%.

SUMMARY

A new heterometric method was presented for the micro-determination of lead with alkali citrate or for the micro-determination of citric acid with lead nitrate. The analysed solution may contain 0.1-1.0 mg of lead or citric acid per one ml. The error lies between zero and 1% in 50% alcoholic solution.

RÉSUMÉ

Les auteurs proposent une nouvelle méthode de microdosage de plomb au moyen de citrate alcalin et inversément un microdosage d'acide citrique au moyen de nitrate de plomb. La solution à analyser doit contenir entre 0.1 à 1.0 mg de plomb ou d'acide citrique par ml. L'erreur est comprise entre 0 et 1% en solution alcoolique à 50%.

ZUSAMMENFASSUNG

Es wird eine neue heterometrische Methode zur Mikrobestimmung von Blei mit Alkalicitrat oder zur Mikrobestimmung von Zitronensäure mit Bleinitrat dargelegt. Die zu analysierende Lösung kann 0.1-1.0 mg Blei oder Zitronensäure pro ml enthalten. Der Fehler liegt zwischen 0 und 1% in 50%iger alkoholischer Lösung.

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A PRECISE HETEROMETRIC DETERMINATION OF CALCIUM IN THE PRESENCE OF LARGE EXCESSES OF MAGNESIUM

by

M. BOBTELSKY AND I. BAR-GADDA

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem (Israël)

The following method makes possible the determination of small quantities of calcium (about 10 mg) in the presence of a large excess of magnesium by means of *one* heterometric titration, which may be carried out in 10-15 minutes at room temperature. The results obtained are accurate within 0.1 mg (1%) or better. The only requirement is that the salt analysed, or its concentrated solution, shall be soluble in ordinary distilled alcohol. This latter condition is easily feasible as both the chlorides and nitrates of the cations concerned are soluble in pure alcohol.

EXPERIMENTAL

All reagents used were either analytical reagents or chemically pure. Although a "Heterometer" (a photometer which is specially constructed for heterometric titrations) was used, many photometers may be adapted for heterometric titrations. (A specially designed "Heterometer" may be supplied if desired). The reaction vessel was a cylinder of about 3.6 cm diameter and the height of the absorption layer was about 1 cm. The suspension obtained must be vigorously agitated during the titration. The phthalate solution was added dropwise from a microburet (0.01 ml). The readings of the galvanometer are made only when they become constant which generally takes a few seconds. The end-point is taken from an enlarged curve. A line is drawn through the maxima optical density points obtained. The point of intersection of the density curve with the maximum density line or the first contact point of both gives the end-point of the titration.

RESULTS

Fig. 1 gives the composition and the results of such a series of heterometric titrations of a constant amount of $Ca(NO_3)_2$ (or $CaCl_2$) in 90% alcohol, which contained increasing quantities of $MgCl_2$, with an alcoholic solution of potassium phthalate. The first maximum optical density point is obtained exactly at the ratio of 1 [Ca] : 1 [Pht] . Generally no further influence of added phthalate is obtained. In solutions which contain 15 times or more molar excess of magnesium, the maximum density point is reached prior to the theoretical value.

As to the absolute maximum optical density values obtained, the following may be said. The values with pure calcium increase with growing Ca-concentration. Besides these values may change with changing room temperature. The series of the titrations shown in Fig. 1 were carried out at a room temperature of about 18° C. A similar series carried out at a later date, at about 25° C gave generally higher maxima optical density values, with the same accuracy in the determination

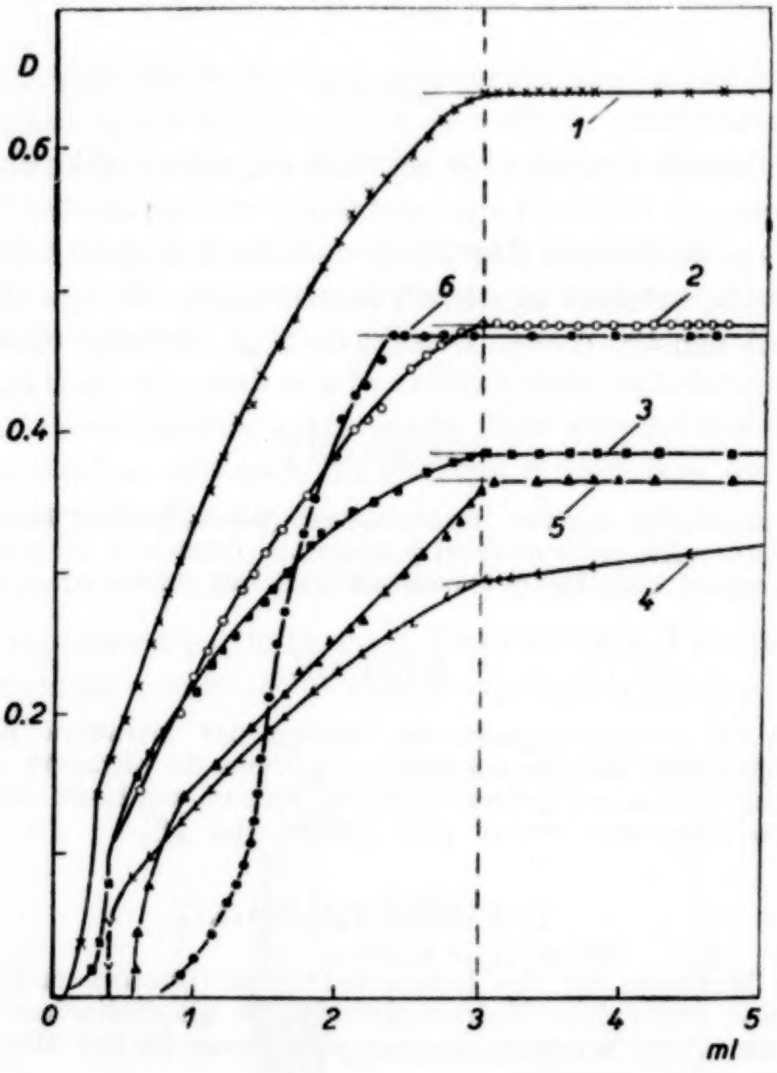

Fig. 1.

1.3 ml $Ca(NO_3)_2$ 0.1 *M* 90 % alc. + 7 ml 90 % alc. + X ml K_2Pht 0.1 *M* 90 % alc.
2.3 ml ,, ,, ,, ,, + 3 ml $MgCl_2$ 0.1 *M* 90 % alc. + 4 ml 90 % alc. + Xml K_2Pht 0.1 *M* 90 % alc.
3.3 ml ,, ,, ,, ,, + 9 ml ,, ,, ,, ,, + Xml ,, ,, ,, ,,
4.3 ml ,, ,, ,, ,, + 2 ml ,, 1 *M* ,, ,, + 5 ml 90 % alc. + Xml ,, ,, ,, ,,
5.3 ml ,, ,, ,, ,, + 3 ml ,, ,, ,, ,, + 4 ml ,, ,, + Xml ,, ,, ,, ,,
6.3 ml ,, ,, ,, ,, + 7 ml ,, ,, ,, ,, + Xml ,, ,, ,, ,,

of calcium as before. The highest value is obtained with pure Ca-solution. With rising Mg-content the values tend to decrease, reaching a minimum value at a certain Mg-concentration. In the highest Mg-concentrations, the maximum density values again approach the values obtained with pure calcium. The accuracy of the calcium determination is of course in no way affected by the absolute maximum optical density values obtained.

The above experimental material shows that a calcium salt which contains big excesses of magnesium may be easily separated from its magnesium content by dissolving the salt in pure alcohol. The precipitation of calcium is then made at room temperature by a dropwise addition of a dilute alcoholic solution of potassium phthalate while stirring vigorously the dilute Ca-solution.

METHOD

10 ml of an alcoholic solution of calcium nitrate or chloride, which contains $\gtrsim$ 10 mg calcium, are titrated heterometrically with an alcoholic solution of 0.1 M neutral potassium phthalate. The latter is added dropwise from a microburet (0.01 ml) while the solution is stirred continuously. The end-point is obtained from the optical density curve. Error: $< 1\%$. Titration time 10-15 minutes.

SUMMARY

A method is presented for the heterometric (photometric) titration (in alcoholic solution) of calcium salts with neutral potassium phthalate. 10 mg of Ca in a tenfold excess of magnesium can be determined with an error of $<1\%$.

RÉSUMÉ

Une méthode est proposée pour un dosage par titration hétérométrique, en solution alcoolique, des sels de calcium au moyen de phtalate de potassium. Des teneurs de 10 mg de Ca en présence de 10 fois ce poids de magnésium peuvent être déterminées avec une erreur plus petite que 1%.

ZUSAMMENFASSUNG

Es wird eine Methode für die heterometrische (photometrische) Titration von Calciumsalzen mit neutralem Kaliumphthalat in alkoholischer Lösung dargelegt. 10 mg an Calcium kann bei einer 10 mal so grossen Menge Magnesium mit einem Fehler $<1\%$ bestimmt werden.

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ÉTUDE DANS LE SYSTÈME MERCURE SOLUTION ACIDE

des Courbes $I = f(E)$ relatives au dépôt et à la redissolution de traces de: Cu, Tl, Cd, Zn, Ni, Co, Fe

par

H. CORIOU, J. HURÉ ET MME N. MEUNIER

Commissariat à l'Energie Atomique, Département de Métallurgie et de Chimie Appliquée, Fontenay-Aux-Roses (France)

Par électrolyse sur cathode de mercure renouvelée[1] il est possible, sous certaines conditions, de déposer quantitativement à la cathode différentes traces de Cu, Tl, Cd, Zn, Ni, Co, Fe contenues par exemple dans des sels d'uranium, de calcium ou de béryllium.

Après avoir distillé, sous courant d'azote, l'amalgame recueilli, nous récupérons en vue de leur dosage les impuretés déposées préalablement sur le mercure.

Afin d'éviter la distillation de l'amalgame nous nous sommes proposés de déterminer les conditions nécessaires à la redissolution quantitative d'un certain nombre d'éléments. Pour réaliser cette étude nous avons tracé dans différents milieux acides les courbes intensité du courant en fonction du potentiel E de l'électrode de mercure ou d'amalgame.

DESCRIPTION DU MONTAGE UTILISÉ

Le montage est représenté par la figure 1. Dans un tube T de section intérieure 3.14 cm^2, nous introduisons 10 ml d'une solution de H_2SO_4 1N et 10 ml de mercure, l'élément à étudier étant dissous suivant l'étude à réaliser dans la solution de H_2SO_4 ou dans le mercure. Le potentiel E de l'électrode de mercure ou d'amalgame est rapporté à celui d'une électrode au calomel saturé reliée par l'intermédiaire

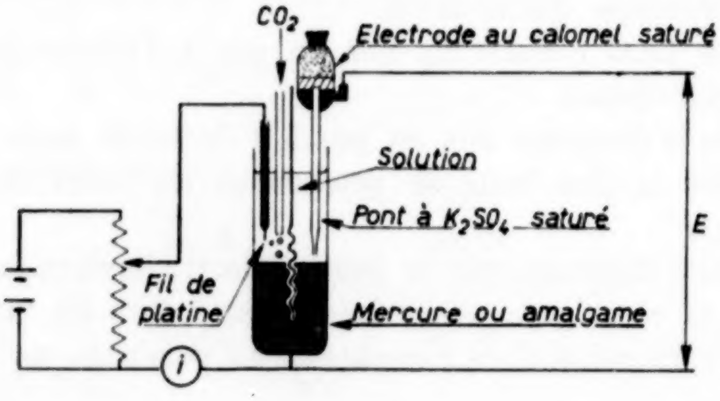

Fig. 1

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d'un pont au K_2SO_4 également saturé; la mesure du potentiel est effectuée à l'aide d'un pH-mètre Philips G.M. 4491 de sensibilité 2 mV. L'intensité i se détermine au moyen d'un galvanomètre de table A.O.I.P. de sensibilité $12.5 \cdot 10^{-9}$ A/mm. Un agitateur brasse en même temps la solution et le mercure.

L'oxygène atmosphérique dissous dans les solutions gênerait dans les mesures, il est donc nécessaire de l'éliminer préalablement par un courant de gaz carbonique, le courant étant maintenu durant toute l'expérience.

Préparation d'un amalgame à concentration donnée

On électrolyse dans une cellule à cathode de mercure renouvelée[1] 100 ml d'une solution de H_2SO_4 1N contenant une quantité connue de l'ordre de 1 à 2 mg du cation que l'on veut amalgamer. Le débit de renouvellement du mercure est réglé de façon à obtenir un volume d'amalgame légèrement inférieur à 10 ml à la fin du temps d'électrolyse requis pour un dépôt quantitatif. Les durées d'électrolyse sont les suivantes pour une densité cathodique de l'ordre de 4 A/cm²:

Tl, Cu = 3 heures
Cd, Co, Fe = 4 heures
Zn = 5 heures.

L'amalgame est recueilli dans le tube T sous un courant de gaz inerte, azote ou gaz carbonique. On jauge ensuite à 10 ml.

ÉQUATIONS DES COURBES DE POLARISATION: $i = f(E)$

Nous utiliserons les notations suivantes:

k et k': constantes dépendant en particulier du choix de l'origine des potentiels et de l'énergie d'activation.
n_T : nombre total d'électrons mis en jeu à l'électrode dans la réaction électrochimique.
n : nombre d'électrons mis en jeu à l'électrode dans la réaction intermédiaire la plus lente se produisant au cours de la "redissolution anodique".
n' : nombre d'électrons mis en jeu à l'électrode dans la réaction intermédiaire la plus lente se produisant au cours du "dépôt cathodique".
a_e : activité du métal dans l'amalgame au voisinage de la surface de l'électrode.
a_e' : activité de l'ion dans la solution au voisinage de l'électrode.
a : activité du métal dans l'amalgame.
a' : activité de l'ion dans la solution.
β : coefficient de transfert relatif à la "redissolution anodique".
α : coefficient de transfert relatif au "dépôt cathodique".

k_d : constante de diffusion du métal dans l'amalgame.
k'_d : constante de diffusion de l'ion dans la solution.

Nous conserverons à F, R et T leur signification habituelle.

Par convention nous donnerons une valeur positive à la densité de courant i relative à la "redissolution anodique" et une valeur négative à la densité i' relative au "dépôt cathodique".

Nous supposerons d'autre part qu'un excès d'électrolyte étranger rend négligeable le nombre de transport du corps électrolysé.

Nous mènerons les calculs en suivant une méthode analogue à celle que GAUGUIN[2] emploie dans le cas d'une réaction où l'oxydant et le réducteur sont sous forme ionique. LEWARTOWICZ[3] dont la publication nous a été connue après la rédaction de ce travail trouve des formules analogues.

Si à un potentiel E, la "redissolution anodique" et le "dépôt cathodique" sont possibles, les deux réactions pouvant être considérées indépendamment l'une de l'autre, les densités de courant correspondantes s'écrivent[4]

$$i = kn_T Fa_e \mathrm{e}^{\frac{\beta nF}{RT}E}$$

$$i' = -k'n_T Fa_e' \mathrm{e}^{\frac{-\alpha n'F}{RT}E}$$

La densité de courant observée I est égale à $i + i'$

$$I = i + i' = n_T F \, (ka_e \mathrm{e}^{\frac{\beta n'F}{RT}E} - k'a_e' \mathrm{e}^{\frac{-\alpha n'F}{RT}E}) \qquad (1)$$

En faisant intervenir les bilans:

$$\frac{i}{n_T F} + \frac{i'}{n_T F} + k'_d \, (a' - a_e') = 0$$

$$-\frac{i}{n_T F} - \frac{i'}{n_T F} + k_d \, (a - a_e) = 0$$

L'équation (1) s'écrit alors:

$$I = \frac{n_T F \, (ka \mathrm{e}^{\frac{\beta nF}{RT}E} - k'a' \mathrm{e}^{\frac{-\alpha n'F}{RT}E})}{1 + \frac{k}{k_d} \mathrm{e}^{\frac{\beta nF}{RT}E} + \frac{k'}{k'_d} \mathrm{e}^{\frac{-\alpha n'F}{RT}E}} \qquad (2)$$

Les limites de cette expression pour $E = +\infty$ et $E = -\infty$ donnent respectivement les densités de courant de diffusion I_d et I'_d dans l'amalgame et dans la solution.

$$I_d = k_d n_T Fa.$$
$$I'_d = -k'_d n_T Fa'.$$

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Réaction irréversible

La Fig. 2 montre la disposition des courbes représentant les variations de la densité de courant en fonction du potentiel E de l'électrode, nous distinguerons successivement les parties suivantes:

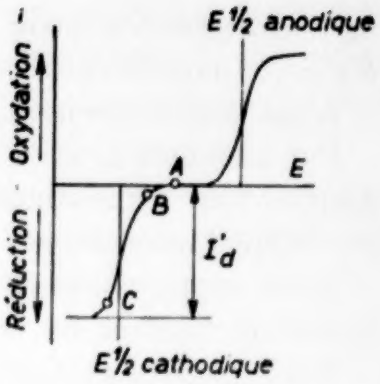

Fig. 2

a) *Partie BC*

Dans le cas de l'irréversibilité nous pouvons, par exemple s'il s'agit du dépôt cathodique, négliger la densité de courant i relative à la redissolution, la constante k devient négligeable et la formule (2) peut s'écrire:

$$I = \frac{-k' n_T F a' e^{-\frac{an'F}{RT}E}}{1 + \frac{k'}{k'_d} e^{-\frac{an'F}{RT}E}} \qquad (3)$$

En introduisant: $I'_d = -k'_d n_T F a'$, l'équation (3) peut se mettre sous la forme:

$$E = -\frac{RT}{an'F} \log \frac{k'_d}{k'} - \frac{RT}{an'F} \log \frac{I}{I'_d - I}$$

$$\text{ou } E = E_{1/2} - \frac{RT}{an'F} \log \frac{I}{I_d' - I} \qquad (4)$$

$E_{1/2}$ représentant la valeur du potentiel pour $I = \frac{I'_d}{2}$

b) *Partie AB*

I est petit vis à vis du courant de diffusion I'_d, c'est à dire que les phénomènes de polarisation de concentration sont négligeables. Nous nous trouvons dans le cas de l'électrolyse idéale.

Dans la formule (3) nous pouvons négliger, devant 1, l'expression

$$\frac{k'}{k'_d} e^{-\frac{an'F}{RT}E} = \frac{I}{I'_d} \qquad \text{d'où} \qquad I = -k' n_T F a' e^{-\frac{an'F}{RT}E} \qquad (5)$$

Réaction "suffisamment réversible"

Si le système est "suffisamment réversible", dans la formule (2) 1 est négligeable vis à vis de $\frac{k}{k_d} e^{\frac{\beta n F}{RT}E} + \frac{k'}{k'_d} e^{-\frac{an'F}{RT}E}$,

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nous obtenons:

$$I = \frac{n_T F\ \left(ka\,\mathrm{e}^{\frac{\beta n F}{RT}E} - k'a'\mathrm{e}^{-\frac{\alpha n' F}{RT}E}\right).}{\frac{k}{k_d}\mathrm{e}^{\frac{\beta n F}{RT}E} + \frac{k'}{k'_d}\mathrm{e}^{-\frac{\alpha n' F}{RT}E}}$$

En introduisant dans cette expression I_d et I'_d:

$$E = \frac{RT}{(\alpha n' + \beta n)F}\log\frac{k'}{k} + \frac{RT}{(\alpha n' + \beta n)F}\log\frac{k_d}{k'_d} + \frac{RT}{(\alpha n' + \beta n)F}\log\frac{I - I'_d}{I_d - I} \qquad (6)$$

La courbe (1) de la Fig. 3 est relative au "dépôt cathodique" d'un élément dont l'activité est nulle dans le mercure. La courbe (2) représente la "redissolution anodique" de ce même élément, son activité étant cette fois nulle dans la solution. Dans les deux cas envisagés, à la différence d'une réaction irréversible, la courbe ne se confond jamais avec la courbe d'électrolyse du corps considéré: la constante de diffusion de l'antagoniste intervient toujours, bien que sa concentration soit infiniment petite dans le système.

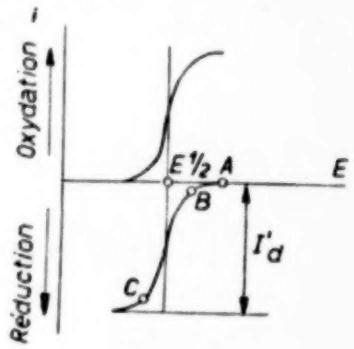

Fig. 3

a) *Partie B'C'*

Si l'activité de l'élément est négligeable dans le mercure, il en est de même de I_d,

$$E = \frac{RT}{(\beta n + \alpha n')F}\log\frac{k'k_d}{kk'_d} + \frac{RT}{(\beta n + \alpha n')F}\log\frac{I'_d - I}{I}$$

$$E = E_{1/2} - \frac{RT}{(\beta n + \alpha n')F}\log\frac{I}{I'_d - I} \qquad (7)$$

b) *Partie A'B'*

Si I est petit devant I'_d, en remplaçant I'_d par $k'_d n_T F a'$ l'équation (7) s'écrit:

$$E = \frac{RT}{(\beta n + \alpha n')F}\left(\log\frac{k_d k'}{k}\,n_T F + \log a' - \log I\right)$$

En posant: $\dfrac{k_d k'}{k} = K$

$$E = \frac{RT}{(\beta n + \alpha n')F}\left(\log K n_T F + \log a' - \log I\right) \qquad (8)$$

Cas intermédiaire

Si la réaction envisagée n'est ni irréversible ni "suffisamment réversible", il est nécessaire d'utiliser la formule (2) complète, E ne peut alors être explicité en fonction de I.

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Sur la Fig. 4, nous avons tracé à 20° les courbes $I = f(E)$ relatives à une solution de H_2SO_4 1*N*. Pour qu'un ion préalablement déposé sur le mercure soit susceptible de repasser en solution sans oxydation du mercure, il est nécessaire que la courbe de redissolution soit située suffisamment à gauche de la courbe d'oxydation du mercure.

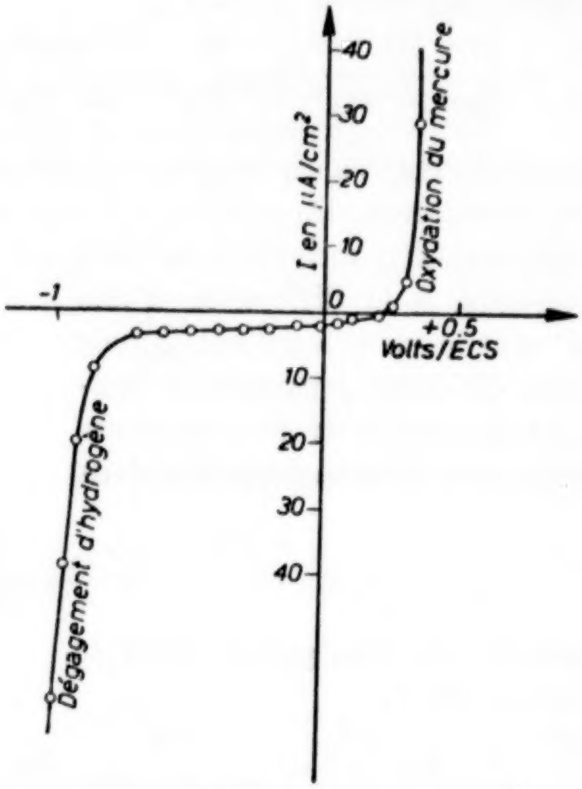

Fig. 4

Résultats obtenus

Les Figures 5, 6, 7 représentent, à 20°, les courbes $I = f(E)$ dans le cas de traces de Cu, Tl, Cd en milieu H_2SO_4 1*N*. Les courbes permettent de vérifier la formule (8), établie lorsque la réaction $M^{+n} + ne \rightleftarrows M$ (amalgame) est réversible et où I est petit vis à vis de I_d.

A 20°, l'équation (8) s'écrit:

$$E = \frac{0.058}{\alpha n' + \beta n} (\log_{10} K n_T F + \log_{10} a' - \log_{10} I)$$

$$\log_{10} I = \frac{\alpha n' + \beta n}{0.058} E + \log_{10} a' + \log_{10} K n_T F \qquad (9)$$

d'où, pour une activité donnée:

$$\log_{10} I = \frac{\alpha n' + \beta n}{0.058} E + \text{constante.} \qquad (10)$$

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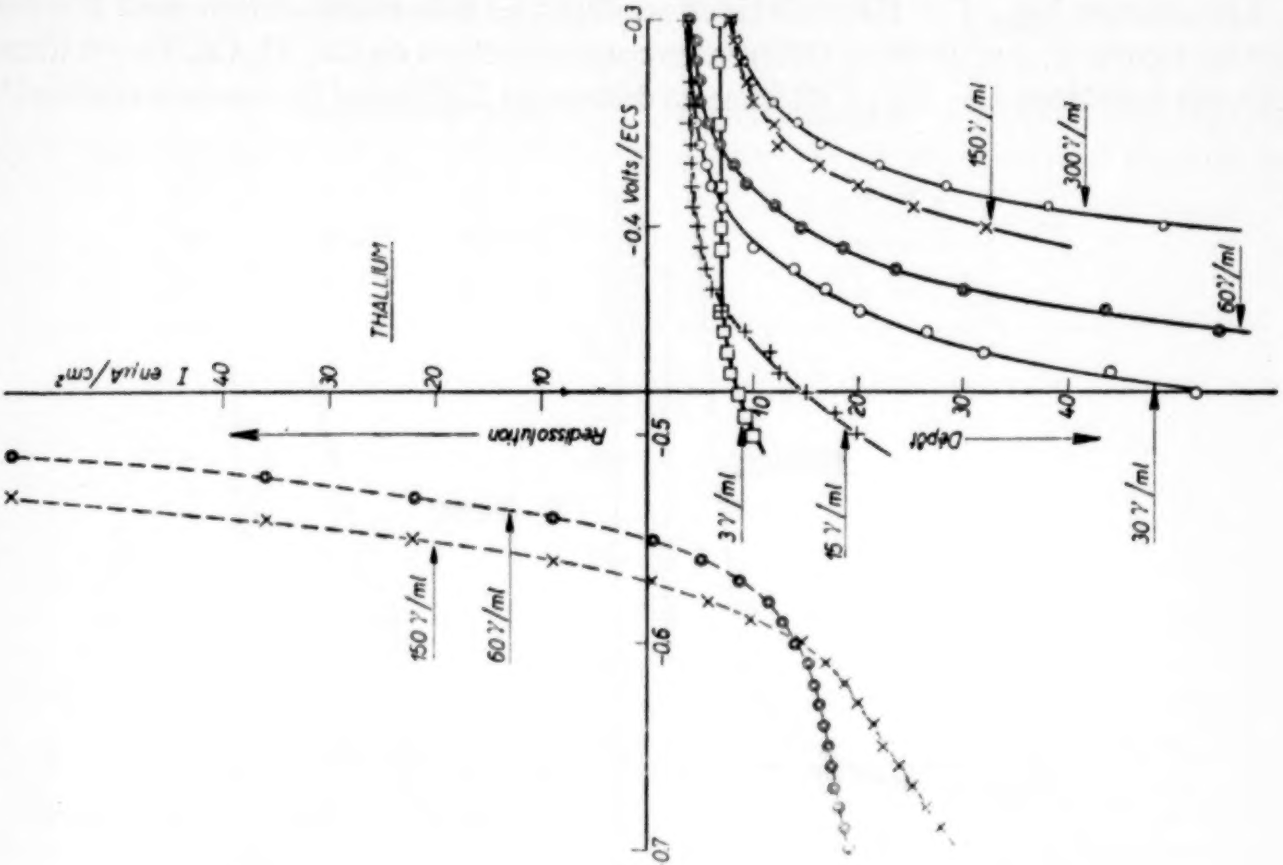

Fig. 6

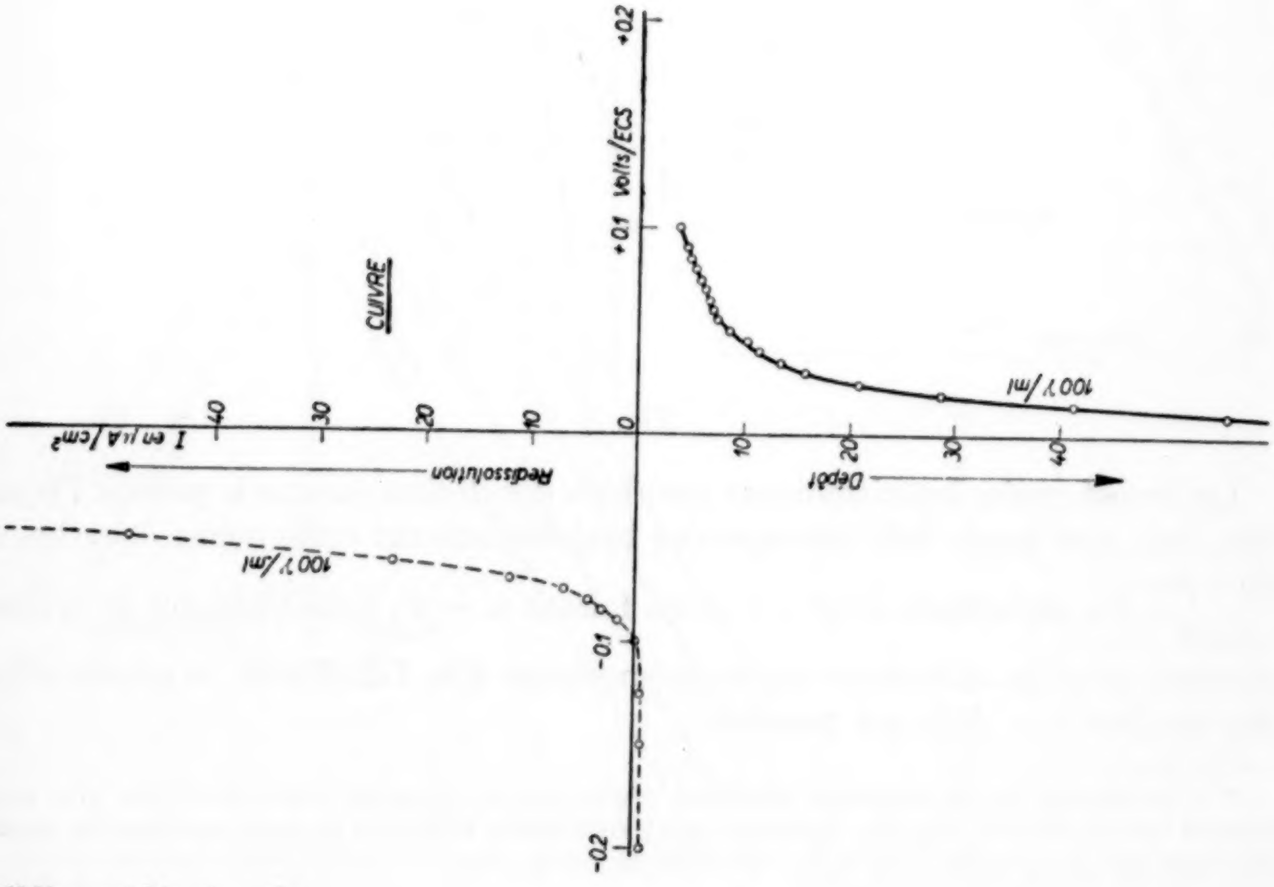

Fig. 5

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Les courbes $\log_{10} I = f(E)$ relatives au dépôt et à la redissolution sont tracées sur les figures 8, 9 et 10 pour différentes concentrations de Cu, Tl, Cd. La vérification des équations $I = f(E)$ s'effectue en déduisant l'intensité du courant résiduel*.

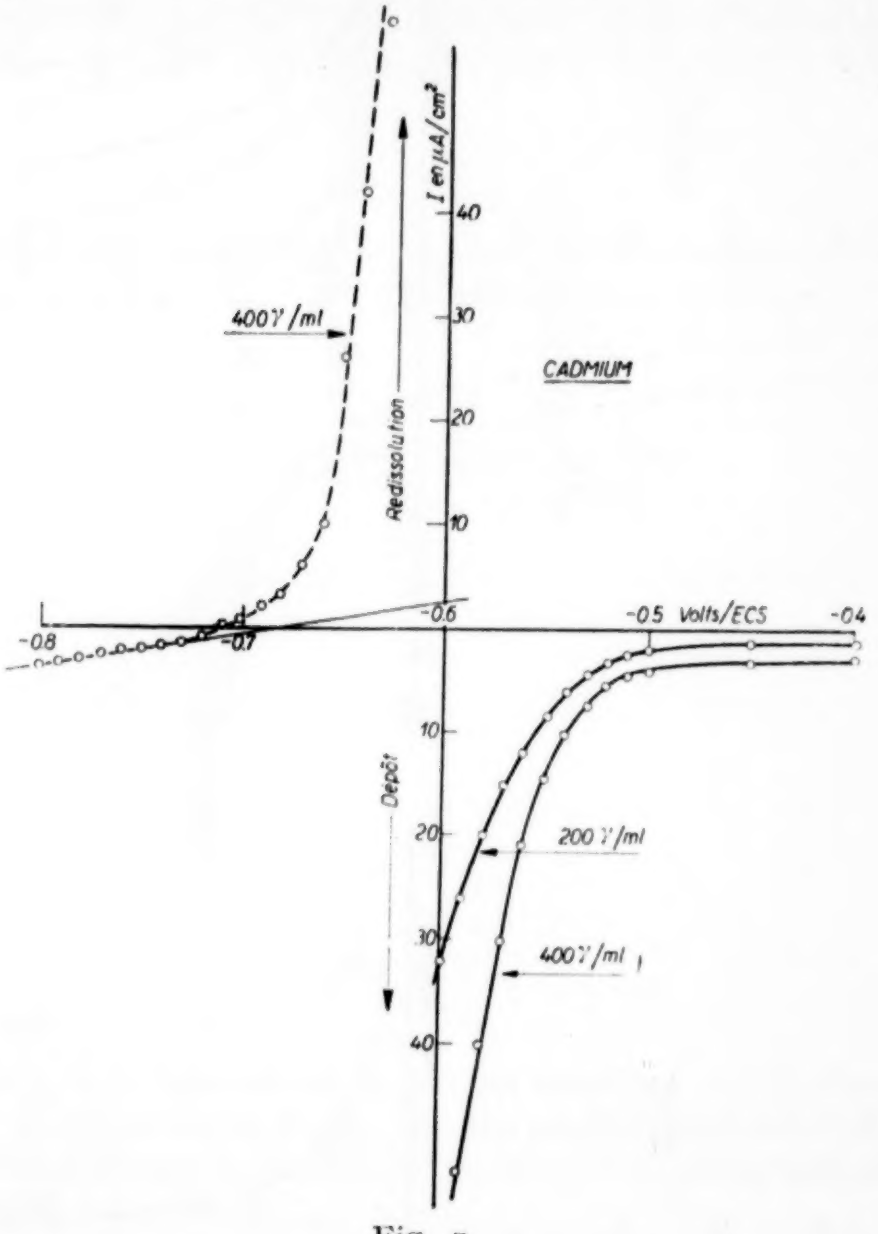

Fig. 7

Les transformées logarithmiques sont bien des droites comme le prévoit l'équation (10); leur pente doit correspondre toujours suivant cette même équation à: $\frac{\alpha n'+\beta n}{0.058}$. En admettant $\alpha+\beta = 1$ et en faisant $n = n'$, nous obtenons le tableau suivant, pour les différents cas expérimentaux (Cu, Cd, Tl) où la construction des courbes $i = f(E)$ est possible:

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* L'intensité de ce courant résiduel n'est pas en général reproductible elle augmente linéairement avec la tension; sa déduction s'effectue en extrapolant la partie linéaire de la courbe $i = f(E)$. (Exemple: Fig. 7).

	Redissolution		Dépôt		
	Valeurs expérimentales		Valeurs expérimentales		
Cu	2.1	$n = 2$	2.2	$n = 2$	
Tl	1.0	$n = 1$	1.1	$n = 1$	
Cd	1.2	$n = 1$	1.0	$n = 1$	

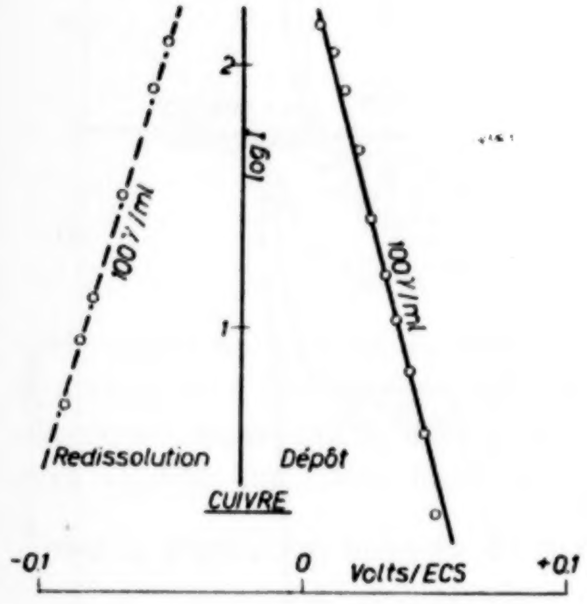

Fig. 8

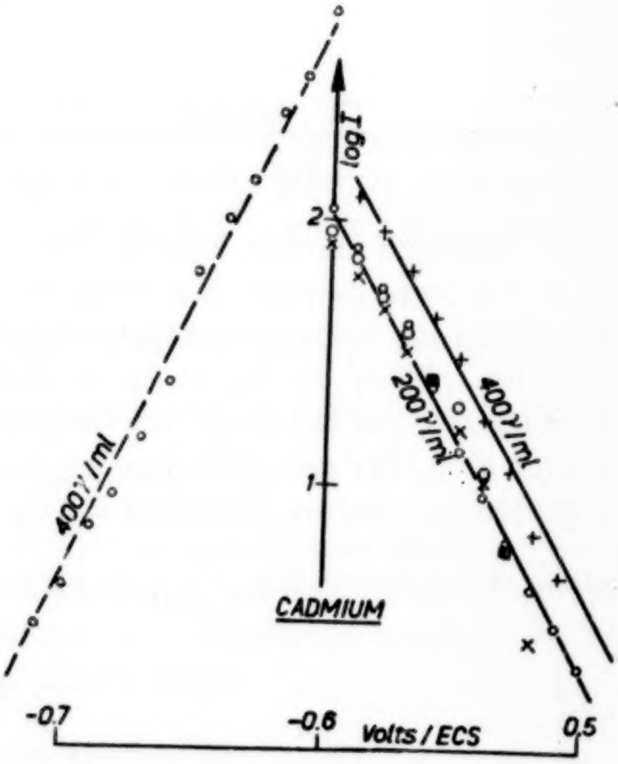

Fig. 9

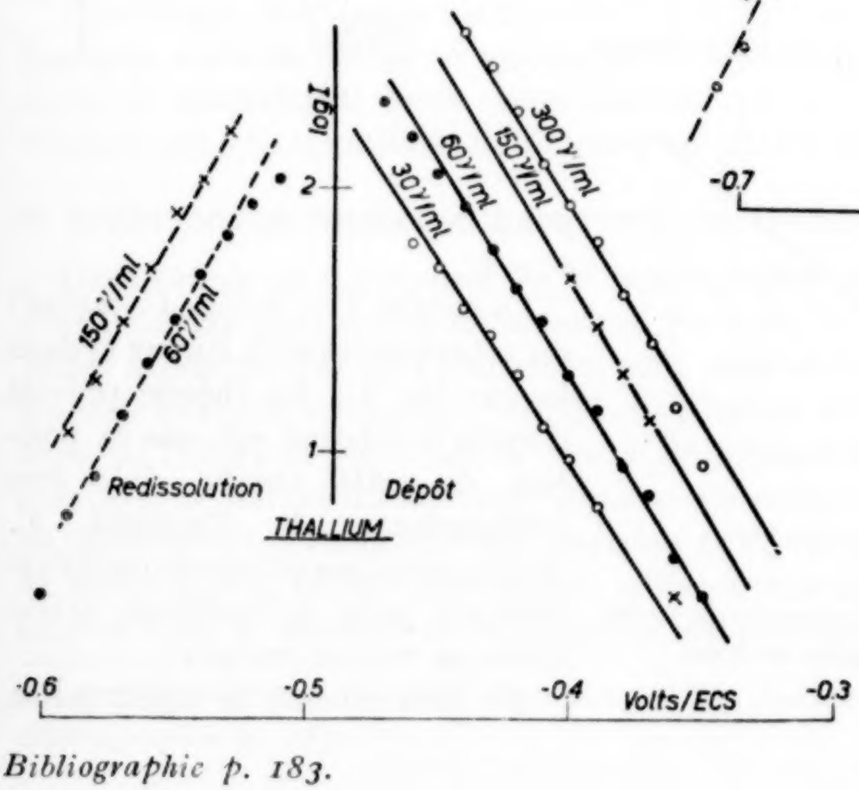

Fig. 10

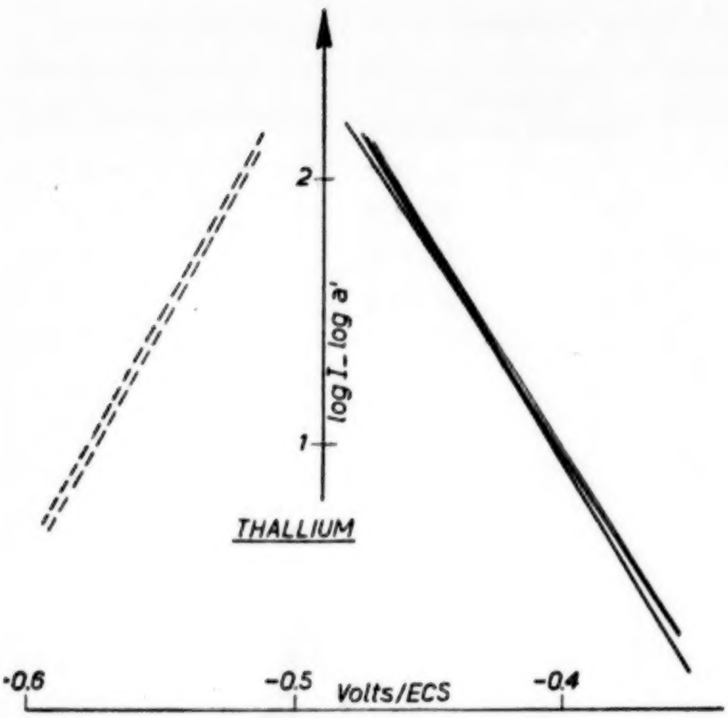

Fig. 11

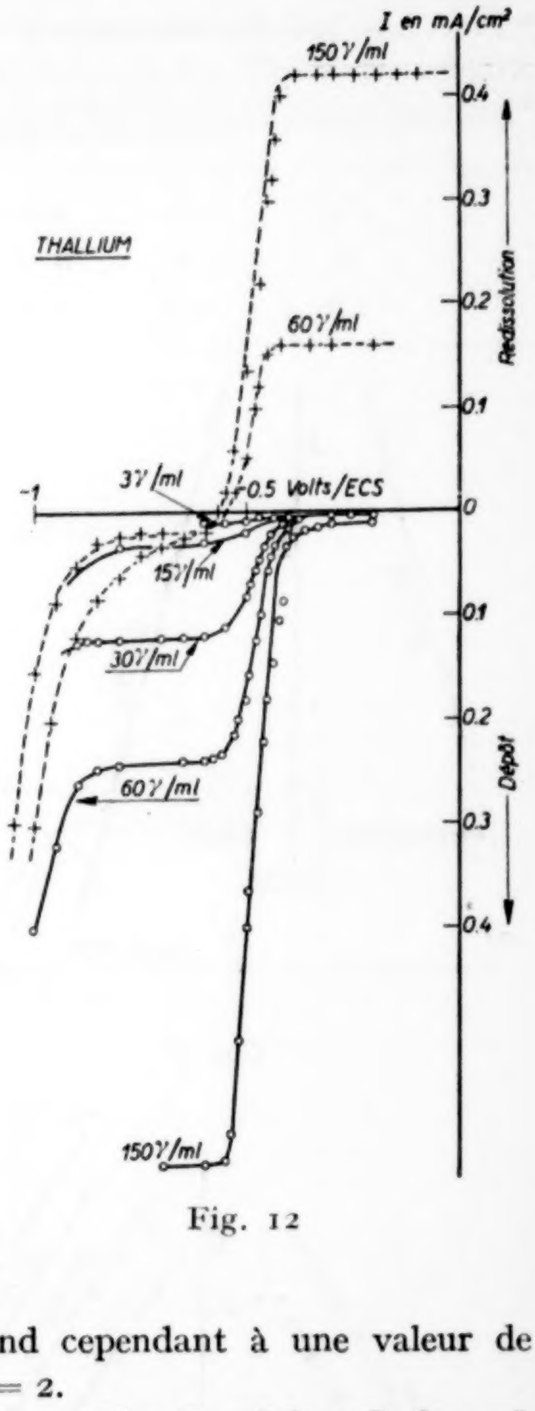

Fig. 12

Le cadmium devrait fournir des valeurs de $n = 2$ correspondant à la mise en jeu de deux électrons. Nous avons répété l'expérience dans les milieux $HClO_4$ et $HCOO\text{-}CH_3$ 1N, dans chaque cas la valeur trouvée pour n est voisine de 1. Par polarographie sur électrode à goutte de mercure en milieu H_2SO_4 1N, la pente de la droite $\log \frac{I}{I_d - I} = f(E)$ correspond cependant à une valeur de $n = 2$.

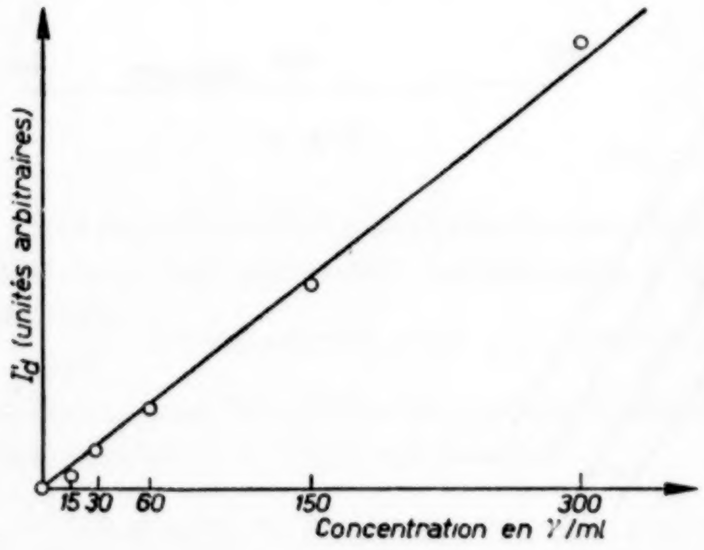

Fig. 12b

La courbe $E = f(\log_{10} I - \log_{10} a')$ est représentée par la Figure 11 dans le cas de Tl. La théorie prévoit d'après la relation (9), que la position de cette courbe doit être indépendante de l'activité a'. Nous constatons qu'aux erreurs d'expérience près, la condition précédente se trouve remplie.

En poursuivant la construction

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des courbes $I = f(E)$, nous obtenons des courbes analogues aux courbes polarographiques sur électrodes à goutte mais où le courant de diffusion est multiplié par un facteur de l'ordre de 300. La Figure 12 montre les résultats trouvés pour le thallium. Nous vérifions approximativement la proportionnalité du courant de diffusion à la concentration en Tl (Fig. 12b). Il est bien évident qu'en raison de la valeur du courant de diffusion, la quantité d'élément déposé au cours de la construction d'une courbe n'est plus négligeable comme pour la polarographie classique. Aussi, pratiquement, la proportionnalité à la concentration ne peut être vérifiée que d'une façon approchée.

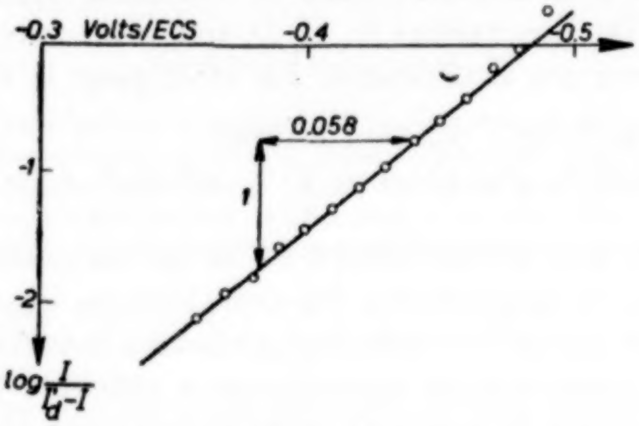

Fig. 13

Sur la Figure 13, nous avons représenté les variations: $\log_{10} \frac{I}{I'_d - I}$ en fonction de E, dans le cas du dépôt de Tl à une concentration de 60 γ/ml. Nous obtenons, en accord avec l'équation (7), une droite de pente $\frac{RT}{nF}$.

Pour le zinc, bien que la réaction $Zn^{+2} + 2e \rightleftarrows Zn$ (amalgame) étudiée à l'oscillographe cathodique[3] ne se montre pas parfaitement réversible en milieu neutre, acide ou ammoniacal, nous avons constaté que la redissolution anodique de cet élément est quantitativement possible en milieu acide.

ESSAIS DE REDISSOLUTION DE TRACES DE Fe, Ni, Co

Dans l'étude qu'il a réalisée sur la polarographie oscillographique HEYROVSKY[5] a montré que dans toutes les solutions Fe^{+2}, Ni^{+2}, Co^{+2} ne présentent pas de palier anodique. Les ions précédents sont donc réduits irréversiblement à l'électrode de mercure. Nous avons vérifié* que pour ces différents ions, à des concentrations de l'ordre de 100 γ/ml, la courbe de redissolution se trouve à droite de la courbe d'oxydation du mercure. Nous avons essayé, en élevant la température, de diminuer l'irréversibilité des réactions précédentes. Des essais effectués à 80° en milieu H_2SO_4 1N ont montré que, même à cette température, il est impossible sans oxyder le mercure de faire passer en solution des traces de Fe, Ni, Co.

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* La vérification a été faite dans les acides: H_2SO_4, $HClO_4$, $HCOO\text{-}CH_3$.

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REMARQUES

1. Sur les courbes de la Figure 12, nous observons pour une même concentration en Tl un palier de diffusion moins élevé dans le cas de la redissolution, le coefficient de diffusion D_s de l'ion Tl dans la solution doit donc être inférieur au coefficient D_a relatif à la diffusion dans le mercure. Or, généralement D_a est un peu supérieur à D_s. Les valeurs D_a et D_s que nous avons relevées dans les tables coïncident avec nos expériences. En effet pour le thallium:

$D_s = 2 \cdot 10^{-5}$ cm^2.sec^{-1} (25°, dilution infinie)
$D_a = 0 \cdot 87$ cm^2.jour^{-1} [6], soit environ 10^{-5} cm^2.sec^{-1} (11.5°)

2. Accessoirement, nous avons étudié à 20° et 80° les courbes $I = f(E)$ pour une solution $1N$ en H_2SO_4, la construction des transformées logarithmiques $\log_{10} I = f(E)$ nous a permis de calculer le coefficient α relatif à la surtension de l'hydrogène sur le mercure. Les transformées logarithmiques obtenues pour 20° et 80° sont parallèles, d'où la nécessité de faire intervenir pour α un coefficient de température que nous trouvons égal à $(2.3 \pm 0.5) \cdot 10^{-3}$ degré$^{-1}$. Ce résultat est en bon accord avec la valeur $2.5 \cdot 10^{-3}$ degré$^{-1}$ calculée par BOCKRIS ET PARSONS[7].

Nous tenons à remercier Monsieur le Professeur CHARLOT qui a bien voulu nous aider de ses conseils.

RÉSUMÉ

Il est possible de faire repasser quantitativement en solution acide et sans oxyder le mercure des traces de Cu, Tl, Cd, Zn préalablement déposées sur mercure; les concentrations envisagées sont de l'ordre de 100 gammas par ml d'amalgame. Dans les mêmes conditions la redissolution quantitative de traces de Fe, Ni, Co ne peut se faire sans oxydation du mercure.

La construction en milieu H_2SO_4, $1N$ des courbes $I = f(E)$ nous a permis de vérifier pour les ions Cu, Cd, Tl, le courant I étant négligeable vis-à-vis du courant de diffusion:

a) la linéarité des variations de log I en fonction du potentiel E de l'électrode de mercure ou d'amalgame.

b) l'indépendance de la position de la courbe: $\log I - \log a = f(E)$ à l'activité a de l'élément dans la solution ou dans l'amalgame.

Nos expériences montrent également:

1° la nécessité d'introduire un coefficient de température pour le coefficient α relatif à la surtension de l'hydrogène sur le mercure.

2° aux faibles densités de courant la mise en jeu pour le cadmium d'un seul électron dans le cas du dépôt et dans celui de la redissolution.

SUMMARY

It is possible to redissolve in acid solution traces of Cu, Tl and Zn previously deposited on mercury without oxidising the mercury; the concentrations considered are of the order of 100γ per ml of amalgam. Under the same conditions the redissolution of traces of Fe, Ni and Co can not be carried out without oxidation of the mercury.

The construction in $1N$ H_2SO_4 medium of the curves $I = f(E)$ for the Cu, Cd and Tl ions, the current I being negligible compared with the diffusion current, shows that:

a. the variations in log I as a function of the potential E of the mercury or amalgam electrode are linear.

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b. the position of the curve log I — log a = f(E) is independent of the activity a of the element in solution or amalgam.

Our experiments also show:

1° it is necessary to introduce a temperature coefficient for the coefficient relative to the overpotential of hydrogen on the mercury.

2° for cadmium, at weak current densities, a single electron is put into play in the case of deposition and in that of redissolving.

ZUSAMMENFASSUNG

Es ist möglich auf Quecksilber abgeschiedene Spuren von Cu, Tl, Cd und Zn quantitativ in saurer Lösung wiederzulösen ohne dabei das Quecksilber zu oxydieren. Die untersuchten Konzentrationen sind in der Grössenordnung von 100 γ per ml Amalgam. Die quantitative Auflösung von Fe-, Ni- und Co-Spuren kann unter den gleichen Bedingungen nicht ohne die Oxydation des Quecksilbers bewerkstelligt werden.

Die Konstruktion der Kurven I = f(E) in 1N H_2SO_4 -Lösung erlaubte uns bei Vernachlässigung der Stromstärke I gegenüber dem Diffussionsstrom für die Cu-, Cd- und Tl-Ionen anzugeben:

a) Die Linearität der Abhängigkeit des log I von dem Potential E der Quecksilber oder Amalgamelektrode.

b) Die Unabhängigkeit der Lage der Kurve log I — log a = f(E) von der Aktivität a des Elementes in der Lösung oder im Amalgam.

Die Ergebnisse unserer Untersuchungen zeigen:

1° Die Notwendigkeit der Einführung eines Temperaturkoeffizienten für den die Wasserstoffüberspannung des Quecksilbers bezeichnenden relativen Koeffizienten a.

2° Bei geringen Stromdichten wird beim Cd nur ein Elektron sowohl bei der Abscheidung wie bei der Wiederauflösung umgesetzt.

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ÉTUDE POLAROGRAPHIQUE DU MERCURE (Hg^{+2}) EN PRÉSENCE D'ACIDE ÉTHYLÈNEDIAMINOTÉTRACÉTIQUE

I. INFLUENCE DU pH SUR LE POTENTIEL DE DEMI-VAGUE — CONSTANTE DE STABILITÉ DU COMPLEXE

par

J. GOFFART, G. MICHEL ET G. DUYCKAERTS

Laboratoires de Chimie Analytique, Université de Liège (Belgique)

SCHWARZENBACH et ses collaborateurs[1] ont fait une étude physico-chimique très approfondie des complexes que l'acide éthylènediaminotétracétique (appelé complexon II) et d'autres réactifs du même groupe, forment avec un grand nombre de cations, et ces données leur ont servi à mettre au point plusieurs dosages volumétriques intéressants.

FURNESS, CRAWSHAW ET DAVIES[2] ont proposé une méthode polarographique de dosage du complexon II basée sur la vague de réduction du complexe cuivrique.

SOUCHAY ET FAUCHERRE[3] ont proposé ce milieu complexant pour le dosage polarographique du cobalt et du fer.

KOLTHOFF ET AUERBACH[4] ont appliqué la méthode polarographique à l'étude des complexes formés entre les sels ferreux et ferriques et le complexon II et ils signalent, à cette occasion, son influence sur la vague anodique de dissolution du mercure.

Etant donné que, à notre connaissance, la constante de stabilité du complexe formé avec le mercure (Hg^{+2}) n'a pas été déterminée, nous nous sommes proposés de la rechercher à partir de l'étude polarographique de la vague d'oxydation du mercure en présence de complexon. Cette méthode avait permis antérieurement à l'un de nous de vérifier la valeur du produit de solubilité du sulfure mercurique[5].

Appareils. Tous les polarogrammes ont été enregistrés à la fois au polarographe Sargent modèle 21 et à l'appareil manuel tel qu'il est décrit dans le traité de polarographie de KOLTHOFF ET LINGANE. Les mesures effectuées au moyen du second appareil étaient destinées aux déterminations précises des potentiels de demi-vague et des courants limites de diffusion.

Toutes les mesures ont été effectuées à 25° ± 0.1 C.

Les pH ont été mesurés au pH-mètre Radiometer.

Tous les enregistrements n'ont pas été faits avec le même capillaire; aussi a-t-il été tenu compte du $m^{2/3} t^{1/6}$, pour la comparaison des courants limites de diffusion.

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L'électrode de référence au calomel saturée en KCl est reliée à la solution à polarographier par l'intermédiaire d'une solution de KNO_3 et de deux points de jonction l'un au KCl et l'autre au KNO_3.

Solutions

1. Les solutions de complexon ont été préparées au moyen du sel disodique de l'acide éthylènediaminotétracétique (SIEGFRIED) et les solutions stock ont été titrées potentiométriquement au moyen d'une solution standard d'hydroxyde de sodium.
2. La solution stock de $Hg(NO_3)_2$ a été préparée en attaquant à l'acide nitrique une quantité pesée de mercure.
3. Les tampons (CLARK ET LUBS) destinés à réaliser les différents pH ont été préparés respectivement au moyen de biphtalate potassique 0.1*M* et KOH 0.1*N*, phosphate monopotassique 0.1*M* et KOH 0.1*N*, acide borique 0.1*M* et KOH 0.1*N* + KCl 0.1*N*.
   Il est à remarquer que NaOH a été remplacé par KOH, (Na^+ est faiblement complexé par le complexon).

Les solutions à polarographier sont préparées en prenant des prises aliquotes de solutions de complexon et de nitrate mercurique, 50 ml de tampon, 2 ml de gélatine à 0.5% et en amenant au volume de 100 ml.

RÉSULTATS EXPÉRIMENTAUX

Vague d'oxydation du Hg en présence de complexon

La dépolarisation anodique par le complexon donne lieu à une vague bien définie dans le domaine de pH où nous avons travaillé (pH 4.5 à 9.5); cette vague se déplace vers les potentiels négatifs lorsque le pH de la solution augmente. En changeant le pH, la forme de la vague demeure inchangée, sauf au delà du pH = 8 où la pente devient plus faible.

Nous donnons, à titre d'exemple, dans la Fig. 1, un polarogramme obtenu au pH de 6.44.

Le potentiel de demi-vague a été corrigé pour la chute ohmique $i\,R$ ($R = 2000\Omega$); la constante du courant de diffusion a été calculée en utilisant la valeur de t au potentiel de + 0.2 volt.vs. S.C.E.

Vague de réduction du complexe mercure-complexon

Une solution contenant des quantités équimoléculaires de Hg^{+2} et de complexon donne uniquement une vague de réduction qui présente les mêmes caractères que la vague de dépolarisation anodique dont nous venons de parler: déplacement de $E^{1/2}$ avec le pH, constante du courant de diffusion sensiblement la même. (voir Fig. 1.)

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Vague composée

Les deux courbes de la Figure 1. révèlent qu'il existe, toutes conditions égales, une légère différence entre les potentiels $E^{1/2}$ de la vague de réduction et de la vague d'oxydation. Comme nous nous proposons de déterminer la constante de stabilité du complexe (mercure-complexon), nous avons estimé utile de rechercher les potentiels d'équilibre d'oxydo-réduction à partir du polarogramme d'une solution contenant à la fois le complexe de mercure et un excès de complexon.

Le point d'intersection du polarogramme avec la courbe du courant résiduel fournit le potentiel d'équilibre d'oxydo-réduction du système.

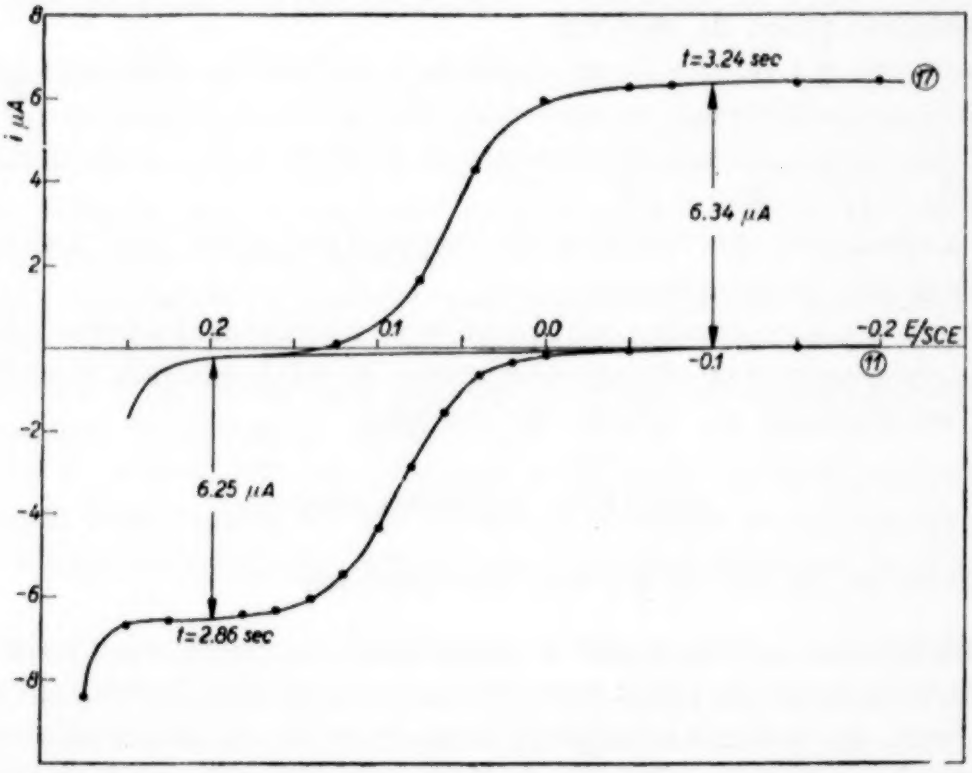

Fig. 1. (11) c(complexon) = 0.996 $10^{-3}M$, pH = 6.44; $E^{1/2} = +0.084$ volt v-s. S.C.E. $E_c^{1/2} = +0.077$ volt; $m = 2.53$ mg sec^{-1}, $t = 2.86$ sec (+ 0.2 volt), $t = 25°$ C, $i_d = 6.25$ μA, $I = \dfrac{I_d}{m^{2/3}\, t^{1/6} .c} = 2.84$.
(17) c(complexe de Hg^{+2}) = 0.996 $10^{-3}M$, pH = 6.36, $E^{1/2} = 0.058$ volt, $E_c^{1/2} = 0.064$ volt; $m = 2.53$ mg sec^{-1}, $t = 3.24$ sec (—0.1 volt), $t = 25°$ C, $i_d = 6.34\,\mu A$, $I = 2.82$.

La Figure 2 illustre quelques résultats obtenus dans un domaine de pH allant de 4.5 à 9.5; nous y avons également représenté la courbe moyenne du courant résiduel.

Les pH et les potentiels d'équilibre d'oxydo-réduction correspondants sont résumés dans les colonnes 2 et 3 du Tableau I.

Etant donné que les vagues se situent dans une région des potentiels où la pente de la courbe électrocapillaire devient importante, il était nécessaire, pour comparer les valeurs des courants limites de diffusion et des constantes de dif-

TABLEAU I

RÉSULTATS EXPÉRIMENTAUX OBTENUS SUR DES SOLUTIONS DE COMPLEXE DE Hg^{+2} + complexon: 0.966 10^{-3} M complexon + 0.482 $10^{-3} M$. Hg^{+2}; 0.01 % gélatine. $t = 25° C + 0.1° C$

No.	pH	$E_{éq}$ volt vs.S.C.E.	$(i_d)_{ox}$ µA/millimole	$I = \frac{(i_d)_{ox}}{C.m^{2/3}.t^{1/6}}$	$(i_d)_{red}$ µA/mill.	$I = \frac{(i_d)_{red}}{C.m^{2/3}.t^{1/6}}$
1	4.60	+0.166	6.30	2.88	6.45	2.87
2	5.00	+0.144	6.16	2.83	6.39	2.85
3	5.55	+0.111	6.35	2.90	6.47	2.88
4	6.00	+0.089	6.35	2.87	6.43	2.85
5	6.42	+0.069	6.39	2.89	6.43	2.86
6	7.00	+0.048	6.25	2.82	6.41	2.84
7	7.49	+0.031	6.24	2.81	6.33	2.80
8	7.97	+0.015	6.16	2.76	6.19	2.74
9	8.36	+0.005	6.26	—	—	—
10	9.09	—0.016	6.14	2.75	5.79	2.55
11	9.64	—0.048	—	—	5.41	2.39

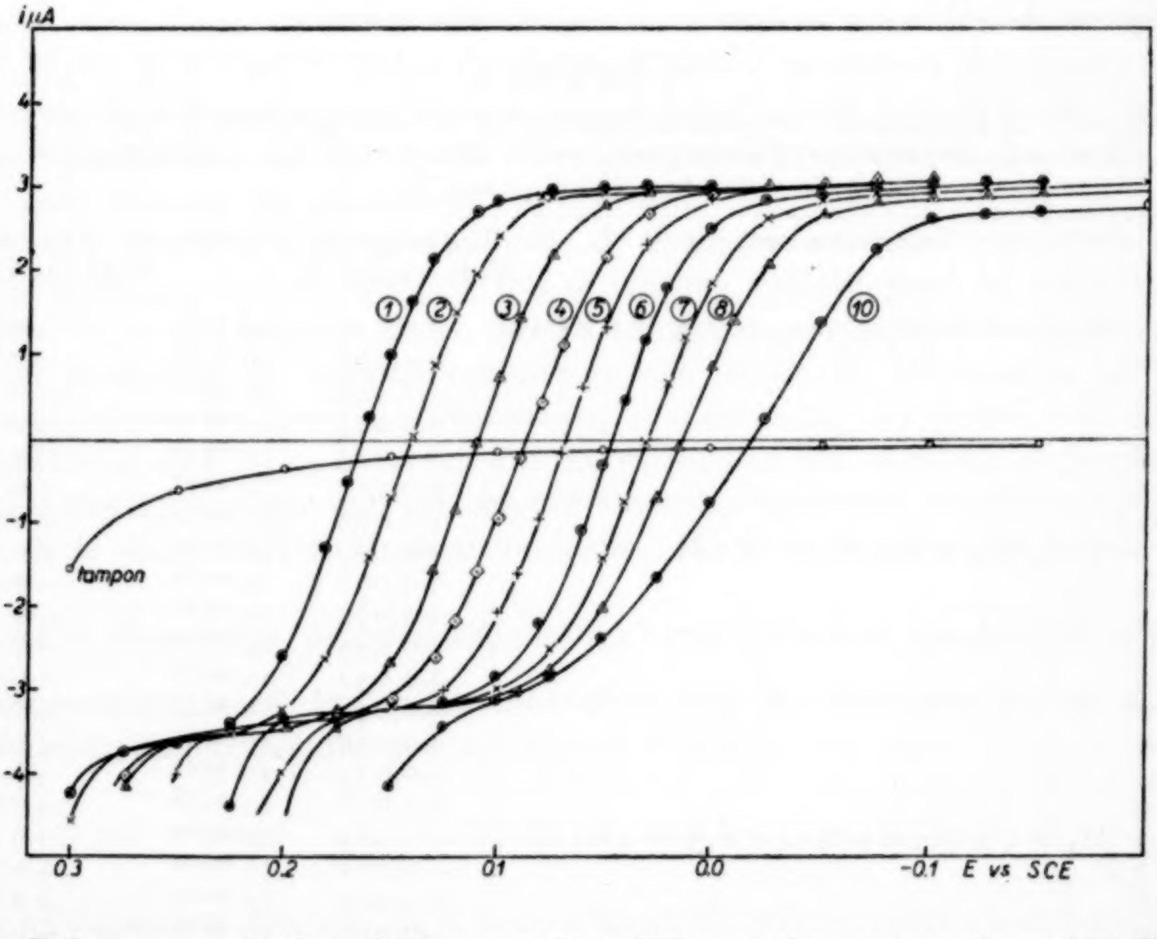

Fig. 2. Polarogrammes de solutions 0.996 $10^{-3} M$ complexon + 0.482 $10^{-3} M$ Hg^{+2}, 0.01 % gélatine, $t = 25° C \pm 0.1° C$.
Les pH et les tampons sont renseignés dans les Tableaux I et II.

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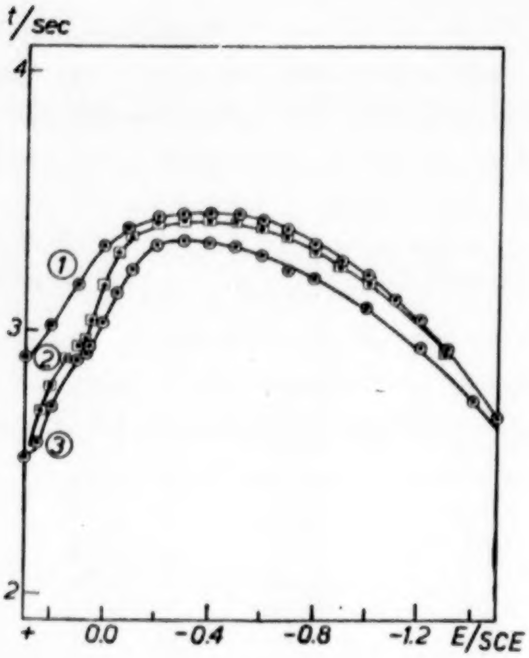

Fig. 3. Courbe électrocapillaire (1) tampon CLARK LUBS, pH = 6.45. (2) idem + $10^{-3}M$ complexon, pH = 6.30. (3) idem + $10^{-3}M$ complexe de Hg^{+2}, pH = 6.20.

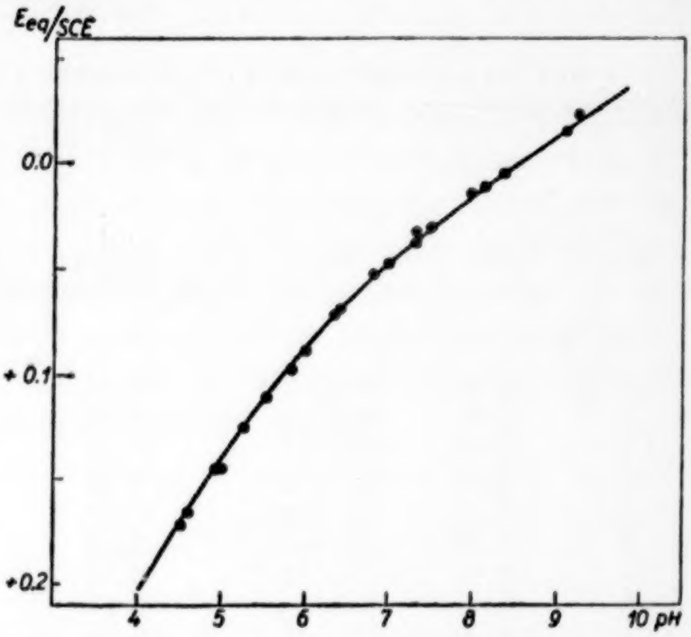

Fig. 4. Courbe des potentiels d'équilibre d'oxydo-réduction du système Hg/Hg^{+2} en présence de complexon.
($t = 25°\,C \pm 0.1°\,C$,) ($\mu = 0.065$)
• Points expérimentaux
— Courbe calculée

TABLEAU II

POTENTIELS D'ÉQUILIBRE D'OXYDO-RÉDUCTION D'UNE SOLUTION CONTENANT LE COMPLEXE (MERCURE-COMPLEXON) AVEC UN EXCÈS DE COMPLEXON

$t = 25°\,C \pm 0.1°\,C$

pH	Tampons employés	$E_{\text{éq}}$ expérim. Volt vs S.C.E.	K Calculé	$E_{\text{éq}}$ calculé Volt vs. S.C.E.
4.54	Biphtalate potassique 0.025 M + KOH	+0.172	$10^{-22.39}$	+0.168
4.60	,, ,, ,,	+0.166	$10^{-22.43}$	+0.164
4.93	,, ,, ,,	+0.145	$10^{-22.50}$	+0.144
5.00	,, ,, ,,	+0.144	$10^{-22.39}$	+0.141
5.28	,, ,, ,,	+0.125	$10^{-22.50}$	+0.124
5.55	,, ,, ,,	+0.111	$10^{-22.47}$	+0.110
5.83	,, ,, ,,	+0.098	$10^{-22.42}$	+0.096
6.00	KH_2PO_4 0.025M + KOH	+0.089	$10^{-22.45}$	+0.087
6.34	,, ,, ,,	+0.072	$10^{-22.51}$	+0.072
6.42	,, ,, ,,	+0.069	$10^{-22.51}$	+0.069
6.82	,, ,, ,,	+0.053	$10^{-22.53}$	+0.054
6.88	,, ,, ,,	+0.052	$10^{-22.51}$	+0.052
7.00	,, ,, ,,	+0.048	$10^{-22.51}$	+0.048
7.30	,, ,, ,,	+0.038	$10^{-22.51}$	+0.038
7.33	,, ,, ,,	+0.033	$10^{-22.65}$	+0.037
7.49	,, ,, ,,	+0.031	$10^{-22.55}$	+0.032
7.97	H_3BO_3 0.025M + KCl 0.025 M + KOH	+0.015	$10^{-22.60}$	+0.018
8.12	,, ,, ,,	+0.012	$10^{-22.54}$	+0.013
8.36	,, ,, ,,	+0.005	$10^{-22.55}$	+0.006
9.09	,, ,, ,,	−0.016	$10^{-22.56}$	−0.015
9.24	,, ,, ,,	−0.023	$10^{-22.65}$	−0.019
	Moyenne	$K = 10^{-22.51 \pm 0.05}$		

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fusion (cathodique et anodique) aux différents pH, de mesurer la courbe électrocapillaire (voir Fig. 3).

Les valeurs des constantes du courant de diffusion ainsi obtenues pour la vague cathodique et la vague anodique se trouvent dans les colonnes 5 et 7 du Tableau II.

Un grand nombre de mesures ont été faites en vue d'obtenir la courbe des potentiels d'équilibre en fonction du pH avec le maximum de précision. L'ensemble des valeurs obtenues est rassemblé dans le Tableau II et reporté sur la Fig. 4.

Tous les polarogrammes ont été obtenus avec les mêmes concentrations des tampons signalés dans le Tableau II.

DISCUSSION DES RÉSULTATS

Constante du courant de diffusion

Nous avons trouvé (Tableau I) qu'aux erreurs expérimentales près, les constantes des courants de diffusion de la réduction du complexe mercurique et de l'oxydation du mercure en présence de complexon sont les mêmes; ce qui signifie que les coefficients de diffusion du complexe mercurique et du complexon sont les mêmes; sans doute, le complexon existe en solution sous différentes formes (H_4Y, H_3Y^-, H_2Y^{-2} HY^{-3}, Y^{-4})et l'équation d'Ilkovic ne permet de calculer qu'un coefficient de diffusion moyen; dans la région de pH allant de 4.60 à 7.97, les formes prédominantes sont H_2Y^{-2} et HY^{-3} et l'on passe progressivement de H_2Y^{-2} à HY^{-3} sans observer de changement appréciable dans la constante de diffusion.

Toutefois, à partir d'un pH de l'ordre de 8, on observe une diminution de la constante du courant de diffusion qui se marque surtout pour la vague de réduction; il est d'ailleurs à noter que la transition correspond au passage du tampon phosphate au tampon borique et une partie du phénomène est sans doute imputable au tampon. Néanmoins, il n'en reste pas moins vrai que la diminution du courant de réduction aux grands pH doit être attribuée en partie à la réaction électrochimique car, on observe simultanément une modification de la pente de la vague indiquant un accroissement de l'irréversibilité de la réaction.

Potentiel de demi-vague, potentiel d'équilibre d'oxydo-réduction, constante de stabilité

SCHWARZENBACH ET ACKERMAN[1] ont déterminé les différents pK de l'acide éthylènediaminotétracétique ($t = 20°$ C, 0.01 N KCl):

$$pK_1 = 1{,}996 \quad pK_2 = 2{,}672 \quad pK_3 = 6{,}161 \quad pK_4 = 10{,}262$$

Ces pK dépendent très fort de la force ionique du milieu; récemment CARINI ET MARTELL[6] ont recherché cette influence. Les calculs qui vont suivre, ont été effectués sur la base des valeurs de SCHWARZENBACH.

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Par analogie avec la formule des complexes d'autres cations bivalents étudiés, nous admettons que la réaction avec le mercure est la suivante:

$$Hg^{+2} + Y^{-4} \rightleftarrows HgY^{-2} \quad \ldots\ldots\ldots\ldots \quad (1)$$

avec la condition d'équilibre:

$$\frac{[Hg^{+2}]\ [Y^{-4}]}{[HgY^{-2}]} = K \quad \ldots\ldots\ldots\ldots \quad (2)$$

Nous allons montrer que cette hypothèse se trouve parfaitement justifiée par nos résultats expérimentaux.

Il est en effet aisé de montrer que le potentiel de demi-vague ($E^{1/2}$), dans le cas de la réaction parfaitement réversible, est donné par la formule suivante:

$$E^{1/2} = E^0 - \frac{0.0591}{2} \log \frac{k_{HgY^{-2}}}{k_{complexon}} + \frac{0.0591}{2} \log K + \frac{0.0591}{2} \log \Theta \quad \ldots \quad (3)$$

$$(t = 25°\ C)$$

dans laquelle $\Theta = \left\{ 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_3K_4} + \frac{[H^+]^3}{K_2K_3K_4} + \frac{[H^+]^4}{K_1K_2K_3K_4} \right\} \quad (4)$

$E°$: potentiel normal du système Hg/Hg^{+2} (0.615 volt vs.S.C.E.)

Nous avons montré précédemment que $k_{HgY^{-2}} \neq k_{complexon}$ à cause de la différence de $m^{2/3}\ t^{1/6}$ pour les vagues de réduction et d'oxydation.

Nous possédons ainsi tous les éléments indispensables pour calculer, au moyen de l'équation (3), la constante de stabilité K du complexe; dans le cas de l'existence simultanée de plusieurs complexes mercure-complexon, on pourra établir l'équation correspondante du potentiel $E^{1/2}$ et utiliser les données expérimentales obtenues aux différents pH pour calculer les constantes de stabilité des complexes.

Si la réaction était parfaitement réversible, le potentiel de demi-vague serait le même que la solution contienne le complexe mercurique seul, le complexon seul ou les deux à la fois. En fait, comme nous l'avons vu, il existe une légère différence entre le potentiel $E^{1/2}$ de la vague de réduction et celui de la vague d'oxydation; ces valeurs encadrent d'ailleurs celle de la vague composée.

Il est donc clair que la réaction décèle une certaine irréversibilité; aussi, nous avons jugé utile de choisir, pour le calcul de la constante de stabilité du complexe, le potentiel $E^{1/2}$ de la vague composée d'une solution contenant des quantités équimoléculaires de complexe de mercure et de complexon en excès. Rigoureusement parlant, nous avons choisi comme potentiel celui du point d'intersection de la courbe polarographique avec la courbe du courant résiduel (c'est à dire le potentiel d'équilibre d'oxydo-réduction); celui-ci est légèrement différent du potentiel de demi-vague (à cause des différences de $m^{2/3}t^{1/6}$ pour les vagues de réduction et d'oxydation).

Pour éviter toute confusion, nous représenterons ce potentiel d'équilibre par $E_{\text{éq}}$.

$$E_{\text{éq}} = 0.615 + \frac{0.0591}{2} \log K + \frac{0.0591}{2} \log \Theta \quad \ldots\ldots\ldots \quad (5)$$

Les valeurs de la constante de stabilité K calculées par la formule (5) dans l'hypothèse du complexe donné par l'équation 1, sont rassemblées dans le Tableau II (4ème colonne).

L'excellente constance de la valeur de K trouvée indique clairement que le complexe formé dans le domaine de pH *étudié (4.54 à 9.24) correspond bien à la formule* HgY^{-2}; *sa valeur moyenne vaut* $10^{-22.15 + 0.05}$.

Cette valeur moyenne de la constante K a servi ensuite à calculer, toujours à partir de la formule (5), la valeur théorique du potentiel d'équilibre ($E_{\text{éq}}$ calculé) et ces valeurs ont servi à tracer la courbe théorique en trait plein de la fig. 4.

Si l'on examine cependant les résultats de très près, (Tableau II et Fig. 4), on remarque que du côté des pH acides, les points expérimentaux se trouvent de façon systématique légèrement en dessous de la courbe théorique. Du côté des pH alcalins, c'est l'inverse; il y a là peut-être l'indication de l'apparition, en proportions faibles à ces pH, d'autres formes de complexes tels que $HgYH^+$ en milieu acide et $HgYOH^{-3}$ en milieu alcalin.

Au cours de la rédaction de ce travail, nous avons eu connaissance d'une étude similaire par MATYSKA ET KÖSSLER[7]; ils ont exploré un domaine de pH allant de 3 à 13 environ, en milieu tamponné et KNO_3 ($\mu = 0.1$); ils ont déterminé le potentiel de demi-vague de la vague anodique; ils mettent en évidence l'existence de trois complexes avec les constantes de stabilité suivantes:

$$HgY^{-2}:10^{-15.7} \qquad HgHY^{-}:10^{-9.0} \qquad HgYOH^{-3} : 10^{-6.8} \; (t = 20^\circ C)$$

Ils trouvent également que dans le domaine de Hg allant 4 à 9, les résultats expérimentaux sont parfaitement représentés par l'hypothèse du seul complexe HgY^{-2}, mais il est important de remarquer que la valeur de la constante de stabilité de ce complexe proposée par ces auteurs est très différente de celle que nous trouvons. La différence ne peut être attribuée à une influence de la force ionique du milieu; nous pensons pouvoir affirmer que notre valeur est exacte et que les auteurs en question ont introduit une erreur systématique dans leurs mesures; nous avons en effet relevé, dans le texte, de leur publication, qu'ils signalent que le potentiel de leur électrode de référence au sulfate mercureux saturée en K_2SO_4 était de 0.417 volt/H_2 alors que la valeur thermodynamique est de l'ordre de 0.65 volt; ils attribuent cet écart à des impuretés métalliques dans le mercure ayant servi à la préparation. Nous pensons qu'il s'agit au contraire d'une erreur de mesure; car, en utilisant la valeur théorique du potentiel de cette électrode au lieu de 0.417, leurs résultats expérimentaux fournissent une constante de stabilité du même ordre de grandeur que celle que nous proposons.

Il y aurait donc lieu de corriger dans le même sens le deux autres constantes proposées respectivement pour le complexe $HgYH^-$ en milieu acide et pour le $HgYOH^{-3}$ en milieu alcalin.

Influence de la force ionique

Nos expériences n'ont pas été faites dans les mêmes conditions de force ionique; la valeur moyenne est de l'ordre de 0.065 avec des limites extrêmes de 0.04 et 0.09.

Dans ces conditions, si l'on corrige la valeur du potentiel normal de Hg/Hg^{+2} de 0.615 volt pour cette force ionique, on obtient 0.604 volt.

En introduisant cette valeur dans la formule (5), on obtient comme valeur moyenne de la constante de stabilité du complexe HgY^{-2} à la force ionique de 0.065: $K_{25°C} = 10^{-22.15 \pm 0.05}$.

CONCLUSIONS

1. Dans un domaine de pH allant de 4.5 à 9.25, le système Hg^{+2} complexon se laisse parfaitement représenter par l'équilibre $Hg^{+2} + Y^{-4} \rightleftarrows Hg_4Y^{-2}$ la constante de stabilité du complexe est égale à $10^{-22.15 \pm 0.05}$ (25° C et $\mu = 0.065$).
2. La vague anodique de dépolarisation par le complexon en milieu tamponné peut être mise à profit pour son dosage; cette méthode nous paraît plus simple et plus immédiate que celle proposée par FURNESS-CRAWSHAW ET DAVIES; la constante du courant de diffusion est égale à 2.86 ± 0.03 ($t = 25°$ C pH: 4.60 à 7.50).

RÉSUMÉ

L'acide éthylènediaminotétracétique (complexon) donne naissance à une vague polarographique anodique de dépolarisation attribuable à la formation d'un complexe stable avec le mercure et dont le potentiel devient plus négatif lorsque le pH augmente.

Le complexe formé entre le complexon et l'ion mercurique est réductible par polarographie, mais son potentiel de demi-vague est légèrement plus négatif que celui de la vague anodique, pris dans les mêmes conditions de pH et de tampons.

L'étude de la variation avec le pH du potentiel d'équilibre d'oxydo-réduction de la vague composée d'une solution contenant des quantités équimoléculaires de complexe et de complexon en excès a permis de montrer que dans le domaine de

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pH allant de 4.50 à 9.25, le seul complexe existant en proportions importantes répond à la formule HgY^{-2}; sa constante de stabilité est égale à $10^{-22.15 \pm 0.05}$ ($t = 25°$ C, $\mu = 0.065$).

La constante du courant de diffusion de la vague de réduction du complexe, comme de la vague anodique de dépolarisation par le complexon est égale à 2.86 ± 0.03 ($t = 25°$ C pH: 4.60 à 7.50).

SUMMARY

The ethylenediaminotetra-acetic acid (complexon) generates an anodic polarographic wave of depolarization to be ascribed to the formation of a stable complex with mercury, and the potential of which becomes more negative when there is an increase in pH.

The complex formed between complexon and the mercuric ion is reducible by polarography, but its half-wave potential is slightly more negative than that of the anodic wave under the same conditions of pH and buffers.

By studying the variation with the pH of the Redox equilibrium potential of the wave constituted by a solution containing equimolecular quantities of complex and complexon in excess, it was possible to show that in the range of pH from 4.50 to 9.25, the only complex existing in considerable proportion corresponds to the formula HgY^{-2}; its stability constant is equal to $10^{-22.15 \pm 0.05}$ ($t = 25°$ C, $\mu = 0.065$).

The constant of diffusion current of the reduction wave of the complex, as well as that of the anodic wave of depolarization by the complexon, is equal to 2.86 ± 0.03 ($t = 25°$ C, pH: 4.60 to 7.50).

ZUSAMMENFASSUNG

Die Äthylendiaminotetracetsäure (Komplexon) erzeugt eine anodische polarographische Depolarisierungswelle welche einer stabilen Komplexverbindung mit dem Quecksilber zuzuschreiben ist und deren Potential mehr negativ wird, wenn man eine Zunahme in pH feststellt.

Die gebildete Komplexverbindung zwischen dem Komplexon und dem Quecksilberion kann durch Polarographie reduziert werden, aber ihr Halbwellenpotential ist etwas mehr negativ als das der anodischen Welle, unter gleichen Bedingungen von pH und Puffern.

Durch das Studium der Variation mit pH des Redox-Gleichgewichtspotentials der Welle, einer Lösung entstehend die äquimolekulare Mengen von Komplex und Komplexon in Überschuss enthält, konnten wir erweisen dass in der pH-Reihe von 4.50 bis 9.25, das einzige Komplex welches in wichtigem Verhältnis erscheint der Formel HgY^{-2} entspricht; seine Stabilitätskonstante ist gleich $10^{-22.15 \pm 0.05}$ ($t = 25°$ C, $\mu = 0.065$)

Die Diffusionstromkonstante der Reduktionswelle des Komplexes, wie die der anodischen Depolarisierungswelle durch das Komplexon ist gleich 2.86 ± 0.03 ($t = 25°$ C, pH: 4.60 bis 7.50).

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BOOK REVIEWS

Papierchromatographie, von FRIEDRICH CRAMER zweite neubearbeitete und erweiterte Auflage, Verlag Chemie, 1953. 136 pages, 68 Fig.,4 coloured plates, price DM 12.80.

This book, like several in the English language (BALSTON AND TALBOT, *A Guide to Filter Paper and Cellulose Powder Chromatography*, BLOCK, LE STRANGE AND ZWEIG, *Paper Chromatography, A Laboratory Manual*), presents the methods of paper chromatography in the form of a handbook for laboratory use.

The author states in the preface that selection of the large literature was necessary and refers the reader to the reviews in *Analytical Chemistry* for a complete bibliography. It is difficult at this stage to decide whether a selection is possible and whether a reader would not profit more from a shorter but complete presentation of the literature.

The general section discusses the evolution of paper chromatography both from adsorption and extraction processes, and the sections on techniques are well written and illustrated.

The technique of paper electrophoresis is also discussed, perhaps with overemphasis on retention analysis.

The special parts are devoted to the numerous groups of compounds separated and contain a large number of R_F tables. The inorganic section is, however, rather poor and confines itself practically to the results of one paper (BURSTALL *et al.*, *J. Chem. Soc.*, (1950) 516).

Some errors were noted by the reviewer:

Under the heading "Two dimensional" the author states that Al_2O_3 impregnated filter paper is used with water as eluant (page 117).

The results of McDONALD *et al.*, on the electrophoresis of Ni and Cu salts have been wrongly presented (page 115).

The method of continuous electrophoresis is credited to GRASSMANN AND HANNIG instead of SVENSSON AND BRATTSTEN (*Arkiv Kemi*, 1 (1949) 401) (p 52).

In the coloured plates, a rather poor two-dimensional amino acid separation, shown in the first edition, has been replaced by a more satisfactory one. Also several inorganic separations from POLLARD *et al.* are shown in colour.

M. LEDERER (Paris)

Physical methods in chemical analysis, par WALTER G. BERL, Volume II, Academic Press Inc. Publishers, New York, 1951. 640 pages.

Le premier volume a paru en 1950. M. STRAFFORD l'a présenté dans *Anal. Chim. Acta*, 5 (1951) 334.

Le second volume qui vient de paraître donne une nouvelle série de méthodes d'analyses physico-chimiques dont certaines sont déjà couramment utilisées dans la pratique.

Chacune de ces méthodes est traitée avec beaucoup de compétence par un spécialiste de la question. On y trouve une partie théorique, une description de l'appareillage et de la technique opératoire et de nombreuses applications pratiques. Les sujets traités sont:

Metallurgical Polarographic Analysis; Polarometric Titrations, by JAROSLAV HEYROVSKY,
Conductometric Analysis, by H. T. S. BRITTON;
Potentiometric Analysis, by H. A. LAITINEN;
Electrography and Electro-Spot Testing, by H. W. HERMANCE AND H. V. WADLOW;
Magnetic Methods of Analysis, by A. R. KAUFMANN;
The Determination of the Area of the Surfaces of Solids, by GEORGE JURA;
Surface Tension Measurements, by MALCOLM DOLE;
Vacuum Techniques and Analysis, by BENJAMIN B. DAYTON;
Gas Analysis by Methods Depending on Thermal Conductivity, by E. R. WEAVER;

The Measurement of Radioactivity for Tracer Applications, by ALOIS OANGER;
Statistical Analysis, by J. SHERMAN;
Chromatographic Analysis, by WALTER G. BERL.

A la fin de chaque chapitre, on trouve une bibliographie fort bien faite, signalant les articles les plus récents et les plus importants.

Ce livre, d'une belle tenue, constitue une mise au point des méthodes modernes d'analyse dont il est souvent difficile de se faire une idée en consultant la profusion d'articles que l'on trouve dans la littérature. Il rendra donc de grands services, tant aux étudiants qu'aux chimistes chevronnés. Il met en relief l'importance et l'élégance de ces nouveaux procédés d'identification et de dosage et permet de se familiariser rapidement avec les appareillages et les techniques nouvelles. C'est une excellente introduction pour ceux qui vont se spécialiser dans le domaine particulier de l'analyse physico-chimique.

Nous ne pouvons donc que le recommander vivement.

D. MONNIER (Genève)

Statistical Methods for Chemists, W. J. YOUDEN, New York, 1951, John Wiley and Sons. 123 p., $ 3.—

Le but de cet ouvrage est de mettre à la portée du chimiste l'utilisation des méthodes statistiques. Contrairement à un préjugé encore répandu il y a quelques années, celle-ci n'oblige pas l'expérimentateur à accumuler une grande quantité de résultats. Au contraire, grâce surtout aux travaux de ,,Student" sur l'étude des petites séries (de deux à vingt résultats environ), on peut dire que les méthodes statistiques ont pour but de permettre à un expérimentateur de tirer le maximum de renseignements d'une quantité limitée de travail; selon l'expression de YOUDEN: ,,Without these statistical tools, scientific conclusions can be drawn, but usually at needless expense of time and material".

L'auteur s'est ici volontairement abstenu de donner aucune démonstration mathématique des théorèmes de calcul statistique qu'il utilise. Par contre, et c'est ce qui fait l'originalité et le très grand intérêt de l'ouvrage, l'auteur connaît parfaitement les difficultés qui peuvent se présenter au chimiste lorsqu'il s'agit de poser correctement un problème, ou d'interpréter correctement les résultats fournis par le calcul; il attire l'attention sur les points délicats qui pourraient échapper aussi bien au chimiste pur qu'au mathématicien pur. En outre, tout au long de l'ouvrage, chaque point traité est illustré par des exemples précis, empruntés à l'expérience quotidienne de l'homme de laboratoire, et traités en détail, y compris les calculs numériques.

Voici les principaux points qui font l'objet d'un exposé concis, mais toujours clair:

Mesure de la précision au moyen de la variance et de l'écart-type; leur estimation dans le cas où on dispose de petites séries de mesures. Détermination des ,,limites de confiance" d'un résultat, notion qui doit remplacer l'ancienne, et vague, notion d',,erreur probable". Comparaison de plusieurs séries de mesures du point de vue de leurs écarts-types et de leurs moyennes (tests t et F). Problèmes liés à l'échantillonnage. Détection des erreurs systématiques constantes. Etude de l'influence d'un ou de plusieurs facteurs sur les résultats (analyse de variance); étude de l'indépendance ou de la dépendance des effets dus à ces différents facteurs (interaction).

L'auteur montre ensuite la nécessité d'un plan de travail correctement conçu pour permettre à l'étude statistique de donner le maximum de renseignements: comment concevoir le programme d'expérience en fonction des renseignements désirés; divers arrangements possibles (carré latin, etc.); moyen d'économiser des expériences en sacrifiant au minimum la précision des renseignements obtenus; expériences où l'on étudie l'influence des variations de deux ou plusieurs facteurs (expériences factorielles); etc. . .

L'étude de cet ouvrage doit être profitable à tous les chimistes, quel que soit leur domaine, et notamment aux chimistes analystes.

DENISE BÉZIER (Paris)

THE INSTITUTE OF PETROLEUM

(26, Portland Place, London, W. 1)

Conference on Applied Mass Spectrometry

A conference on applied mass spectrometry organized by the Mass Spectrometry Panel of the Institute of Petroleum Hydrocarbon Research Group is to be held in London on Thursday and Friday, 29 and 30 October, 1953. The venue of the Conference is the Institution of Electrical Engineers, Savoy Place, London, and its main object is to bring together American, British, and European workers in the field of applied mass spectrometry to discuss problems of current and future interest. The majority of papers are designed to interest those who use mass spectrometers in their daily work, but all of the papers on the first day are devoted to subjects in analytical chemistry where mass spectrometry has proved particularly valuable. It is hoped that these papers will give rise to discussions between mass spectrometrists and those who carry out similar analyses by alternative methods.

In all there will be 18 papers from workers in the U.K., the U.S.A., Canada, France, Germany, and Holland, and these will cover broadly: -

1. Quantitative analysis of gases, liquids and solids, including the continuous monitoring and control of product composition by mass spectrometry;

2. Applications to the study of molecular structure, free radicals, and electron/molecule collision processes;

3. Recent developments in instrumentation and computing techniques.

In order to cover the cost of papers and other conference expenses a registration fee of £2 2s. 0d. will be charged. Applications for further particulars and for registration forms should be made to W. J. BROWN, c/o Metropolitan-Vickers Electrical Co. Ltd., Trafford Park, Manchester 17, as soon as possible.

NOTE RELATIVE TO THE PAPER OF F. L. HAHN: FÜR EINE KORREKTE DARSTELLUNG DER pH-LEHRE

by

J. EECKHOUT

Laboratory of Analytical Chemistry, University, Ghent (Belgium)

In a previous paper[1] we have derived a general equation for the calculation of hydrogen ion concentration in salt solutions:

$$[H^+]^2 = \frac{\{[K_1[A_1^+] + K'_1[B_2^-] + K_w]\}\, K_2}{K_2 + [B_2^-]}$$

K_1 is the acidity constant of the cation (acid);
K_2 is the acidity constant of the conjugate acid of the anion (base);
K'_1 is the acidity constant of the anion (ampholyte), for the special case we have an acid salt;
$[A_1^+]$, $[B_2^-]$ are the concentrations of the ions A^{+b} and B^{-a}, resulting from the dissociation of the salt A_aB_b in aqueous solution.

As can be stated one approximation was introduced in the derivation of this general formula: the neglect of activity coefficients, putting concentrations for activities.

In subsequent discussions conditions were given under which certain quantities in the general equation can be neglected. This results in the derivation of approximated relations for several special cases. It is striking that simplified relations are identical with those which have been independently derived by classical methods for salts from a weak acid with a strong base, a weak base with a strong acid, a weak acid with a weak base, acid salts, and ampholytes.

Hence one single formula is applicable in any case, and separate equations for salts of different types as mentioned above need not be derived.

In a recent paper HAHN[2] turns special attention to the correlation between acids and bases, as a direct consequence of the Brönsted concept of acids and bases. He shows that the different constants, which characterize the dissociation of acids and bases and the hydrolysis of cations and anions, can be advantageously replaced by one single value, *i.e.* the "equilibrium constant" of the acidoid basoid system.

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This results also in a remarkable simplification in the calculation of pH values, since many of the actual formulae disappear and only four are retained: one for acids, one for bases, one for ampholytes and a fourth for buffer mixtures.

Conditions are given for which the remaining approximated formulae can be applied. Where accuracy obtained from those is insufficient, a more accurate value is obtained from the method of repeated approximations.

HAHN complains of the lack of explanation for the designations used in the derivation of the general formula in our previous paper, and states that the calculation of pH from the different approximated relations, even if followed by repeated computations, is much more convenient than the application of one general formula, which should decompose into a number of simple relations for practical application. Moreover, some values calculated from the general equation above are cited as less accurate.

If we accept the Brönsted concept of acids and bases, we assume that all (hydrated) cations react as acids, all anions react as bases, because they can take up protons. Hence in a solution of the salt A_aB_b, which dissociates in *a* cations A^{+b} and *b* anions B^{-a}, the cation A^{+b} is the acid of the system:

$$A^{+b}_{n.aq} \rightleftharpoons H^+ + (A_{(n-1)aq}OH)^{+(b-1)}$$

the anion B^{-a} is the base of the system:

$$B^{-a} + H^+ \rightleftharpoons HB^{-(a-1)}$$

In aqueous solution we shall consider also the acid-base systems of the ampholyte solvent:

$$H_2O_{(acid)} \rightleftharpoons H^+ + OH^-$$

$$H_2O_{(base)} + H^+ \rightleftharpoons (H_3O)^+$$

Hence the total reactions should be:

$$A^{+b}_{n.aq} + H_2O \rightleftharpoons (H_3O)^+ + (A^+{}_{(n-1)aq}OH)^{+(b-1)}$$

$$B^{-a} + (H_3O)^+ \rightleftharpoons H_2O + HB^{-(a-1)}$$

Equilibrium equations, however, are not changed, and it is a general practice to write H^+ instead of $(H_3O)^+$.

Further, if, for a solution of a salt A_aB_b, we denote by A^+ the cation (acid), and by B its conjugate base, by B^- the anion (base) and by A its conjugate acid, without regard to the valency of ions, the acid-base systems involved can be expressed by the simple equations:

$$A_1{}^+ \rightleftharpoons H^+ + B_1,\ \text{equil. const. } K_1$$

$$A_2 \rightleftharpoons H^+ + B_2{}^-,\ \text{equil. const. } K_2$$

If, however, we have an acid salt, the anion B^- is an ampholyte: it is the base of its conjugate acid A, and it is an acid with a conjugate base B^{-2}. We write B^{-2} because the conjugate base must have a valency that is always more negative by one unit. For this particular case we shall consider a third acid-base system:

$$B_2^- \rightleftharpoons H^+ + B_2^{-2}, \text{ equil. const. } K'_1$$

These three simple equations have been used in the derivation of the general formula.

It is obvious from the above that K_2 is the acidity constant of the conjugate acid of the anion (base) in the solution. We never use basicity constants. It is a direct consequence of the Brönsted concept that acids and bases of each conjugated system are fully characterized by one single constant, although this was never explicitly stated. This is first done by HAHN[2], who calls this constant the ,,equilibrium constant" of the system.

As to the application of equations the following considerations will be made here:

First, it is not always easy to know which of the approximated formulae can be applied with the greatest accuracy, and the rules given by HAHN are insufficient in many cases: A solution of an acid salt most generally reacts as an ampholyte, but can react also as an acid or as a base, depending on concentration and equilibrium constants of the acid-base systems involved. For a solution of NaH_2PO_4, 0.1*M*, — a typical acid salt — pH can be calculated from the approximated relation:

$$\text{pH} = \tfrac{1}{2}\,(\text{p}K_1 + \text{p}K_2)$$

When the concentration is 0.001*M* or less, the solution behaves practically as if only the weak acid $H_2PO_4^-$ were present, and the formula for weak acids will give a more accurate result. For a solution of Na_2HPO_4, 0.1*M*, good results are obtained with the formula for ampholytes, but a 0.001*M* solution behaves practically as a solution of the weak base HPO_4^{-2}, and hence, the appropriate equation shall be used.

This has first been shown by FLOOD[3], and is derived directly from the general formula, as has been shown in our previous paper.

Other difficulties can arise:

$(NH_4)_2HPO_4$ can be considered either as an acid salt or as the salt from the weak acid $H_2PO_4^-$ with the weak base NH_3. Simplified relations for the calculation of pH of both types of salts are identical, and HAHN classifies them all as "ampholytes". This is correct, and can be concluded also from our paper, where no difference is made between both types. However, in the particular case here, the constants K_1 and K_2, which are put in the approximated relation, differ for both cases. Writing the general formula it will be obvious that the pH can be calculated as for a solution of NH_4Ac, *i.e.* $(NH_4)_2HPO_4$ should be considered as the salt from a weak acid with a weak base. In the "ampholyte" $(NH_4)_2HPO_4$ we consider the 2 acid-base systems:

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \quad , \ldots . K_1 = 10^{-9.2}$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}, \ldots K_2 = 10^{-7.2}$$

and not the systems:

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}, \ldots K_1 = 10^{-7.2}$$
$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}, \ldots . K_2 = 10^{-12.3}$$

Hence, $pH = \frac{1}{2}(9.2 + 7.2) = 8.2$

Even in the special case where none of the systems above can be neglected, the general equation gives the correct resolution.

On the other hand, the application of the method of repeated approximations causes no difficulty whatever when we have a solution of an acid or a base, it is less convenient, however, for a solution of an ampholyte. Moreover, there is not a single indication that the approximated relation should be no longer applicable, and solutions to which the simplified relations retained by HAHN can not be applied are numerous. On the contrary, writing the general equation, the limited range of applicability of simplified relations is properly defined, and the formula which can be used with greatest accuracy in each particular case is derived in a very simple manner.

Furthermore, the general formula is not at all complicated, and derivation is not difficult, even easier than the derivation of the classical approximated relation for ampholytes. Application is very easy also in most practical cases. The derivation of approximated relations has shown that all classical formulae have only a very limited range of applicability. It is, however, not necessary at all to formulate these approximated relations, because they are derived from the general equation by neglecting some minor quantities, which is a simple mathematical operation. Hence, writing the general equation and substituting convenient values for $[A_1^+]$ and $[B_2^-]$, accurate results will always be obtained, and any admissible approximation can be applied if desirable.

Where accuracy is concerned, it is unlikely that a general equation, derived without introducing any assumption, except the neglect of activity coefficients, should be less accurate than simplified relations derived from the former by making several approximations, as is insinuated by HAHN.

As to the pH values, calculated from the general formula, for solutions of Na_2SO_4, 0.1*M*, and $NaHSO_4$, 0.01*M*, and quoted by HAHN as inaccurate, it can be pointed out that:

1. In the derivation of approximated relations, and in the particular case that $K_1 \ll K_2$, the concentration of the cations A_1^+ and of the anions B_2^- has been put equal to the initial concentration, since these ions are almost weak acids and weak bases, and quantitative dissociation of salts A_aB_b is assumed.

However, *it has been stated explicitly that there are some exceptions for which this approximation can not be justified, and that attention should be drawn to these*[1]. One of these exceptions is $NaHSO_4$, for which the approximated relation leads to a abnormal pH value of 1.85 for a $0.01M$ solution, because HSO_4^- is not a weak acid and $[B_2^-]$ can not be put equal to the initial concentration C. This has been noticed in accordance with the explicit statement mentioned above, and the accurate solution has been given in a subsequent remark. The actual value* found is 2.14 (and not 2.00 as asserted by HAHN). Indeed, only for strong acids as HCl we put $pH = -\log C$, and find $pH = 2$ for a $0.01M$ solution. Equilibrium constant of the acid HSO_4^- is $K = 10^{-1.7}$. Hence, dissociation is not complete and pH is higher than 2.00.

Apart from that, the same value 2.14 (and not 2.0) should be obtained from the formula for acids given by HAHN, since the only difference in the two methods is this: where we put $[H^+]$ as the unknown in the correct relation and resolve the resulting equation of second degree, HAHN gives $[H^+]$ a definite approximated and repeats the calculation until the value found is nearly the same as the tried value.

Moreover, following strictly the indications in the paper of HAHN, pH of a solution of $NaHSO_4$, a typical "acid salt", should be calculated from the formula given for ampholytes:
$pH = \frac{1}{2}(pK_1 + pK_2)$. As H_2SO_4 is a strong acid, with $K_1 > 1$, and $K_2 = 10^{-1.7}$, an even more abnormal value than 1.85 would be obtained. Application of the general formula shows without ambiguity that the pH for solutions of this salt should be calculated from the formula for weak acids. This illustrates in a particular manner the great utility of the general equation.

2. Although the general admitted opinion regards Na_2SO_4 as a "neutral" salt, some difference of a solution of this with a solution of KCl is striking. Indeed, while the latter is the salt of the strong base KOH with the strong acid HCl, the former is the salt of the strong base NaOH with the acid HSO_4^- ($K = 10^{-1.7}$). HSO_4^- is not as strong an acid as HCl, and is rather comparable with H_3PO_4 ($K_1 = 10^{-2}$). Hence a solution of Na_2SO_4 will not be neutral in the same sense as a solution of KCl, and the value calculated from the general equation seems most acceptable. This has been confirmed by the following experiment:

A solution of Na_2SO_4 $0.1M$ (II) has been compared with a solution of KCl of the same ionic strength (I). Two identical quinhydrone electrodes have been introduced, one in each solution, and connection is realized by a salt bridge with a saturated solution of KCl. The potential difference is measured with a Leeds and Northrup potentiometer, the electrode dipping in the KCl solution being connected with the positive pole. We found for this cell a potential difference of 0.027 V with solutions prepared with ordinary distilled water, and 0.028 V when freshly boiled and cooled water was used. Hence, neglecting liquid junction potentials — the influence will be small in the given conditions —, it follows that:

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* We remember that all values are calculated without introducing activity coefficients. Hence the value 2.09, given by HAHN and calculated with activities, is not taken into consideration.

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$$E_{(I)} - E_{(II)} = -0.059\ \mathrm{pH}_{(I)} - (-0.059\ \mathrm{pH}_{(II)}) = 0.028$$
$$\text{or, } \mathrm{pH}_{(II)} - \mathrm{pH}_{(I)} = 0.47$$

The pH of a solution of Na_2SO_4 $0.1M$ is higher than this of a solution of KCl of the same ionic strength by approximately half a unit, and, therefore it can hardly be said that Na_2SO_4 is a "neutral" salt. This agrees with the value calculated from the general equation.

SUMMARY

Some objections to the general equation derived for the calculation of pH of salt solutions, and published in a previous paper, are confuted, and the utility of the general relation is shown by treating some special cases.

It is pointed out that the accuracy of results obtained is rather good in any case. Some values, questioned by HAHN, have been confirmed experimentally.

It is recorded that the application of the general equation is very easy in most practical cases.

RÉSUMÉ

Quelques objections à la formule générale, formulée pour le calcul du pH d'une solution d'un sel et communiquée dans un article précédent, ont été réfutées, et l'utilité de la formule est montrée en traitant quelques exemples.

On a montré que la précision des résultats obtenus est très satisfaisante. Certaines valeurs trouvées, mises en doute par HAHN, sont confirmées expérimentalement.

L'application de la formule générale est en outre très facile.

ZUSAMMENFASSUNG

Einige Einwände zu der für die Berechnung des pH's von Salzlösungen abgeleiteten und in einer früheren Arbeit veröffentlichten allgemeinen Gleichung wurden widerlegt und die Nützlichkeit dieser allgemeinen Beziehung wurde an der Behandlung einiger spezieller Fälle gezeigt. Es wird darauf hingewiesen, dass die Genauigkeit der erhaltenen Ergebnisse in jedem Fall ziemlich gut ist. Einige Werte, die von HAHN in Frage gestellt wurden, wurden experimentell bestätigt. Die Anwendung der allgemeinen Gleichung ist, wie berichtet wird, in den meisten praktischen Fällen sehr einfach.

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THE APPLICATION OF THIOSALTS IN ANALYSIS
II. ESTIMATIONS BASED ON DECOMPOSITION OF THIOSALTS
Part B. ESTIMATION OF MOLYBDENUM AND TIN

by

I. K. TAIMNI AND R. P. AGARWAL

Chemical Laboratories, University of Allahabad, Allahabad (India)

In an earlier publication[1], the authors dealt with the quantitative estimation of arsenic, tellurium and selenium as sulphides and it was shown that the precipitates obtained on the decomposition of the thiosalts of these metals correspond exactly with the formulae of the sulphides, providing thereby a satisfactory method for their estimation. An effort was made to apply the method for the estimation of other metals which form thiosalts and it was found that satisfactory results could be obtained for molybdenum and tin also.

With these two metals the precipitate of the sulphide obtained on decomposing the thiosalts cannot be heated before weighing because it loses weight continuously on heating. The heating of the precipitate in both the cases was completely eliminated by washing the precipitate with water, alcohol and ether successively and finally drying it in a vacuum desiccator. The weight of the precipitate obtained under these conditions was constant and was directly proportional to the amount of the metal present in the solution. The weight of the metal could thus be easily calculated by multiplying the weight of the precipitate by a constant factor. On examining these factors it was found that they corresponded exactly with the formulae $MoS_3.2H_2O$ and $SnS_2.2H_2O$.

EXPERIMENTAL

Estimation of molybdenum

The gravimetric determination of molybdenum by precipitating it as sulphide and igniting the sulphide to oxide is not considered to be a good method and is confined to the determination of very small amounts of the metal. Not only is the complete precipitation of the sulphide a difficult matter as pointed out in Part I of this series[2] but the ignition of MoS_3 to MoO_3 should be carried out in a "muffle" according to BRINTON AND STOPPEL[3]. The method based upon the decomposition of the thiosalt as outlined below is much simpler and is applicable to fairly large amounts of the metal.

A pure sample of ammonium molybdate was dissolved in water and the amount of molybdenum in the solution was determined by precipitating it with 8-hydroxyquinoline[4] or lead acetate[5]. Measured volumes of the molybdate solution were treated with an excess of about 15 N ammonium sulphide or 2N sodium sulphide solution, about 15 ml of the alkali sulphide solution being required for every 50 mg of molybdenum. The solution containing the thiosalt was treated with excess of dilute hydrochloric acid until the colour of the thiosalt was completely discharged and the metal was precipitated as sulphide. The mixture was heated to boiling, allowed to settle, filtered through a weighed Gooch or sintered glass

TABLE VIII

WITH 2N SODIUM SULPHIDE REAGENT

No.	Vol. of Mo solution in ml	Vol. of reagent added in ml	Vol. of 2N HCl added in ml	Wt. of Mo sulphide in g	Wt. of Mo in the ppt in g	Wt. of Mo actually present
1	25	10	35	0.0204	0.00859	0.00859
	25	8	30	0.0205	0.00863	
	25	5	30	0.0204	0.00859	
2	25	12	40	0.0903	0.03802	0.03799
	25	15	45	0.0902	0.03798	
	25	20	50	0.0903	0.03802	
3	25	15	40	0.1188	0.05003	0.04994
	25	15	45	0.1187	0.05000	
	25	20	50	0.1190	0.05011	

TABLE IX

WITH CONCENTRATED AMMONIUM SULPHIDE REAGENT

No.	Vol. of Mo solution in ml	Vol. of reagent added in ml	Vol. of 6N HCl added in ml	Wt. of Mo sulphide in g	Wt. of Mo in the ppt in g	Wt. of Mo actually present in g
1	25	5	25	0.0204	0.00859	0.00859
	25	8	30	0.0203	0.00855	
	25	10	30	0.0204	0.00859	
2	25	15	40	0.0902	0.03798	0.03799
	25	12	40	0.0903	0.03802	
	25	15	45	0.0901	0.03794	
3	25	10	30	0.0638	0.02686	0.02685
	25	12	35	0.0637	0.02682	
	25	12	35	0.0638	0.02686	

crucible (porosity 4) washed with water, alcohol and ether successively, dried in a vacuum desiccator for half an hour and weighed. The sulphide precipitate should be sucked dry at the filter pump for about 15 minutes before being placed in the desiccator. The ratio: weight of the metal/weight of the precipitated sulphide was always found to be 0.4211 corresponding exactly with the formula $MoS_3.2H_2O$. The results obtained in different experiments are given in Tables VIII and IX.

Estimation of tin

The gravimetric determination of tin by first precipitating[6] it as sulphide and then converting the sulphide to oxide involves many difficulties and is avoided as far as possible. The solution, after treatment with hydrogen sulphide, has generally to be kept overnight, the slimy character of the precipitate makes filtration and washing very difficult, and the conversion of the sulphide to the oxide, in spite of the elaborate precautions taken, is uncertain. As compared with the above method the determination of tin by decomposing the thiosalt and weighing the precipitated sulphide is remarkably simple and takes very little time as the following procedure adopted in our experiments will show.

A pure sample of metallic tin was dissolved in concentrated hydrochloric acid and treated with bromine water to oxidize the tin to the stannic form. The solution of stannic chloride was standardized by precipitating the tin with cupferron[7] or ammonia[8] and ignition of the precipitate to stannic oxide. Measured volumes of the stannic chloride solution were treated with ammonium hydroxide until a white precipitate of stannic hydroxide began to appear and then with a large excess of $2N$ sodium sulphide, about 15 ml of the alkali sulphide solution

TABLE X

WITH $2N$ SODIUM SULPHIDE REAGENT

No.	Volume of Sn solution in ml	Vol. of reagent added in ml	Vol. of $3N$ acetic acid added in ml	Wt. of sulphide in g	Wt. of Sn in the ppt in g	Wt. of Sn actually present in g
1	10	6	20	0.0353	0.01915	0.01914
	10	8	25	0.0353	0.01915	
	10	10	25	0.0352	0.01910	
2	25	15	45	0.0731	0.03967	0.03962
	25	20	50	0.0730	0.03960	
	25	20	50	0.0728	0.03954	
3	25	15	45	0.0883	0.04790	0.04785
	25	20	50	0.0881	0.04780	
	25	20	50	0.0882	0.04785	

being required for every 50 mg of the metal. The white precipitate of the stannic hydroxide dissolved giving a yellowish solution of sodium thiostannate. This was then decomposed by the addition of excess of 2-3*N* acetic acid giving a yellowish-white voluminous precipitate which changed to brown on washing with alcohol and ether and drying. Acetic acid gives a denser precipitate than hydrochloric acid and is to be preferred. The precipitate was allowed to stand for ten minutes, filtered through a weighed Gooch or sintered glass crucible, washed with water, alcohol and ether successively, sucked dry at the filter pump for 15 minutes, dried in a vacuum desiccator for about an hour and weighed. In this case the ratio: weight of metal/weight of precipitated sulphide is 0.5427 corresponding exactly with the formula $SnS_2.2H_2O$. The existence of $SnS_2.2H_2O$ has already been reported by SHEERER. The results are given in Table X.

Behaviour of vanadium, gold and platinum

These three metals are precipitated completely by the decomposition of their thiosalts as pointed out in a previous paper[2]. In view of the success obtained in the quantitative estimation of arsenic, tellurium, selenium, molybdenum and tin we tried to apply the method for the estimation of vanadium, gold and platinum also. But the results obtained in the case of these three metals showed that the method could not be applied to them in the simple form in which it is applicable to the other metals. A more rigorous study of the conditions of precipitation of the sulphides from the thiosalts may, however, show that the general method is applicable to these metals also. Further work with these metals is progressing.

SUMMARY

1. It has been shown that molybdenum can be precipitated quantitatively by adding excess of concentrated ammonium sulphide to a molybdate solution and then decomposing the thiosalt with excess of hydrochloric acid.

2. The weight of the precipitate corresponds to the formula $MoS_3.2H_2O$ and the quantity of metal can be estimated by multiplying the weight of the precipitate by a constant factor.

3. The same method is also applicable to the gravimetric estimation of tin. The precipitate of stannic sulphide is easily filterable and its weight corresponds to the formula $SnS_2.2H_2O$.

4. The general method in its simple form has not been found to be applicable to vanadium, platinum and gold.

RÉSUMÉ

1. Il est démontré que le molybdène peut être précipité quantitativement par addition d'un excès de solution concentrée de sulfure d'ammonium à une solution de molybdate, puis par décomposition du thiosel formé au moyen d'acide chlorhydrique en excès.

2. Le poids du précipité correspond à la formule $MoS_3.2H_2O$, et la teneur en molybdène peut être déterminée en multipliant ce poids avec un facteur approprié.

3. Cette méthode peut également être utilisée comme dosage gravimétrique de l'étain. Le précipité de sulfure stannique se filtre bien et son poids correspond à la formule $SnS_2.2H_2O$.

4. Cette méthode générale ne peut pas s'appliquer au vanadium, au platine et à l'or.

ZUSAMMENFASSUNG

1. Es wurde gezeigt, dass Molybdän durch Hinzufügen eines Überschusses von konz. Ammoniumsulfid zu einer Molybdatlösung und Zersetzung des Thiosalzes mit einem Überschuss von Salzsäure quantitativ ausgefällt werden kann.

2. Das Gewicht des Niederschlags entspricht der Formel $MoS_3.2H_2O$ und die Menge des Metalls kann durch Multiplikation des Gewichtes des Niederschlages mit einem konstanten Faktor bestimmt werden.

3. Die gleiche Methode ist ebenfalls zur gravimetrischen Bestimmung von Zinn anwendbar. Der Zinn-IV-sulfidniederschlag ist leicht zu filtrieren und sein Gewicht entspricht der Formel $SnS_2.2H_2O$.

4. Die allgemeine Methode in ihrer einfachsten Form liess sich nicht auf Vanadium, Platin und Gold anwenden.

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THE APPLICATION OF THIOSALTS IN ANALYSIS
III. A NEW SCHEME OF QUALITATIVE ANALYSIS — PART A

by

I. K. TAIMNI AND R. P. AGARWAL

Chemical Laboratories, University of Allahabad, Allahabad (India)

In the paper[1] entitled "Complete precipitation of Sulphides" it was shown by the authors that the three metals, molybdenum, platinum and arsenic, which are precipitated with great difficulty by hydrogen sulphide from an acid solution, can be precipitated easily and completely by adding excess of concentrated ammonium sulphide and then decomposing the thiosalts which are formed with excess of hydrochloric acid. Vanadium, which normally is not precipitated with the copper-arsenic group, can also be completely precipitated with the arsenic group under these conditions.

The precipitation of sulphides by decomposing the thiosalts was further studied quantitatively[2,3] and it was shown that the decomposition of thiosalts with the complete precipitation of sulphides could be utilized for the gravimetric estimation of arsenic, selenium, tellurium, molybdenum and tin. It was also shown that in the case of three other metals examined, *viz.*, vanadium, platinum and gold, though the metals can be precipitated completely as sulphides it is not possible to estimate them gravimetrically by weighing the precipitate.

The ease with which thiosalts can be formed by adding a large excess of concentrated ammonium sulphide solution and the complete precipitation of sulphides from such solutions has not only made easy the gravimetric estimation of many metals as sulphides but has also opened up the possibility of simplifying to a considerable extent the scheme for the detection of basic radicals in mixtures containing common as well as the so-called "rare" elements.

Many schemes dispensing with the use of hydrogen sulphide have been put forward from time to time, but as DOBBINS AND SOUTHERN[4] have shown "no scheme dispensing with the sulphide ion which would equal the sulphide scheme of FRESENIUS in efficiency has yet been put forward or is likely to be put forward". This is so because the values of the solubility products of hydroxides, carbonates, sulphates, and phosphates are decidedly less satisfactory from the analytical point of view as compared with the solubility products of sulphides.

The use of organic reagents, which is finding increasing application in inorganic qualitative analysis, while excellent for bringing about separations of particular metals after they have been separated into groups by other reagents, can hardly be applied in our present state of knowledge for the separation of metals into groups. Even if such a scheme based on the use of organic reagents alone could be devised it would hardly be suitable for students learning the technique of qualitative analysis on account of the complexity of reactions shown by the organic reagents and the difficulty and cost of procuring them for routine class work.

The most useful line of approach in improving the scheme of qualitative analysis for the basic radicals will thus seem to be to retain the use of the sulphide ion in the separation of metals into groups and to eliminate as completely as possible all those features of the old scheme[5] which make it inconvenient, combersome and time-consuming. The formation of thiosalts and their decomposition with the precipitation of sulphides was, therefore, studied by us very thoroughly with a view to finding out whether the classical scheme of qualitative analysis could be modified in such a manner that all the advantages of using the sulphide ion are retained and at the same time the procedure is simplified to a great extent. As a result of these studies it has been shown that it is possible to devise a new scheme in which the valuable features of the classical scheme are retained and the chief objectionable features are eliminated.

The following are some of the advantages of the new scheme:

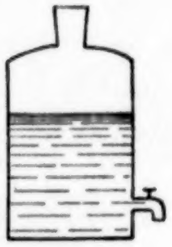
1. The use of the hydrogen sulphide gas with all its obnoxious features is completely eliminated and the gas is replaced by a convenient reagent — concentrated ammonium sulphide solution.
2. The time taken in precipitating the sulphides from an acid solution, which may be more than an hour, is reduced to about five minutes and the precipitation is not only very convenient but also more complete.
3. The separation of the copper group from the arsenic group is far more satisfactory than in the method involving the use of yellow ammonium sulphide.
4. The total time taken in completing the analysis for the basic radicals is reduced considerably.
5. As the main features of the new scheme are similar to those of the classical scheme[5] the student who has been trained in the old technique can take to the new method without much difficulty.

Before giving the details of the new scheme, it would be desirable to give a broad outline of the general procedure which is adopted and the important points which have to be noted.

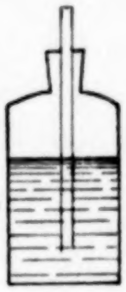
Preparation of the reagent. As the new scheme is based upon the use of concentrated ammonium sulphide instead of hydrogen sulphide gas a few details may be given here concerning the preparation and storage of this reagent.

The reagent is prepared by saturating ordinary liquor ammonia, which has preferably been cooled in ice, with hydrogen sulphide gas from a Kipp'sapparatus. If this reagent is kept exposed to atmospheric oxygen it gets quickly oxidized and a yellow colour of polysulphide, gradually increasing in intensity, develops in the solution. An effective method of preventing undue oxidation is to pour some liquid paraffin in the bottle. This forms a layer at the top of the reagent and prevents its further oxidation. A light yellow colour may, however, develop but this does not increase in intensity and does not interfere with the action of the reagent. The ammonium sulphide reagent can be conveniently stored in a container fitted with a stop-cock near the bottom (Fig. a). It can then be taken out from the container without any difficulty and the reagent can also be replenished by pouring more of the freshly prepared ammonium sulphide from the top. If, however, it is desired to provide the reagent on all the shelves in a class room it may be kept in ordinary reagent bottles with a paraffin seal as mentioned above. In this case the best method of taking out the reagent from the bottle will be to use a glass tube with a wide bore of about 0.5-1.0 cm as shown below (Fig. b):-

a



b



If hydrogen sulphide gas is passed into a single bottle containing ammonium hydroxide a considerable proportion of it is lost. A number of bottles containing ammonia may, therefore, be connected in series and the loss thus minimized to a great extent.

Procedure I

As the mixture is not likely to be soluble in water or dilute acids the first step in analysis according to the new scheme is evaporation of the mixture with concentrated nitric acid and hydrochloric acid successively, to dissolve out all the soluble constituents. The residue is taken up with dilute hydrochloric acid, treated with bromine water, drop by drop, to oxidize tin and thallium, filtered hot and washed several times with hot water. The precipitate will contain all the insoluble substances while the filtrate will contain the soluble salts of all the metals that may be present in the mixture. The insoluble substances that may generally be found in the insoluble residue are $AgCl$, $AgBr$, AgI, $BaSO_4$, $SrSO_4$, $PbSO_4$, Al_2O_3, SnO_2, Sb_2O_4, HgS, SnS_2, CaF_2, SiO_2, WO_3, TiO_2, $Zr(OH)PO_4$, and complex ferro-cyanides and have to be tested for separately by a special method. If the mixture has been subjected to the treatment mentioned above, all the mercury will be present in the mercuric form, lead will pass into the filtrate as $PbCl_2$, thallium will be oxidized and pass into the filtrate as $TlCl_3$, and silver and tungsten will form part of the insoluble residue as AgCl, and WO_3, respectively. The silver group of the classical scheme is thus completely eliminated in the new scheme and the separation into groups begins with the addition of concentrated ammonium sulphide to the acid solution.

Procedure II

The acid solution containing the basic radicals is treated with concentrated ammonium sulphide reagent until strongly alkaline. The mixture is stirred thoroughly and filtered. The precipitate of hydroxides and sulphides is extracted once with concentrated ammonium sulphide to ensure complete solution of sulphides which form thiosalts, and the second filtrate is added to the first. The precipitate is then washed thoroughly with hot water and the washings are also added to the combined filtrate. The precipitate contains the hydroxides and sulphides of metals like mercury, lead, titanium and zirconium and the filtrate the thiosalts of metals like arsenic, tin, molybdenum as well as alkaline earth metals and alkalis.

Procedure III

The solution containing the thiosalts is boiled with excess of concentrated hydrochloric acid, and filtered. The concentration of acid in the resulting mixture should be about 6*N* in order that the sulphides of arsenic and platinum may be completely precipitated, and those of antimony and tin may dissolve completely. The precipitate contains those metals of the arsenic group whose sulphides are insoluble in 6*N* hydrochloric acid. The filtrate will contain the chlorides of antimony, tin, alkaline earth metals, alkalis and traces of vanadium which may have escaped precipitation with concentrated acid. The detailed analysis of the precipitate is dealt with in Part B of this paper.

Procedure IV

The filtrate containing antimony and tin is treated with concentrated ammonium sulphide reagent until the precipitate of antimony and tin sulphides which may form dissolves in the excess of the reagent. The resulting solution is treated with excess of dilute hydrochloric acid and filtered. If the filtrate from *Procedure III* has a light blue colour owing to the presence of traces of reduced vanadium it should be first treated with hydrogen peroxide before adding ammonium sulphide reagent. Hydrogen peroxide oxidizes the vanadium and ensures its complete precipitation as sulphide along with antimony and tin. The detailed analysis of the precipitate and the filtrate is treated in Part B of this paper.

Procedure V

The precipitate obtained in *Procedure II* which contains the insoluble hydroxides and sulphides is treated with cold dilute ($1N$) hydrochloric acid for 2-3 minutes, the mixture is stirred and filtered immediately. The treatment with cold dilute acid dissolves out all the hydroxides except that of thallium and all the sulphides except those of mercury, lead, bismuth, copper, cadmium, as well as nickel and cobalt. The filtrate will contain the chlorides of cerium, thorium, iron, manganese, (thallium), titanium, zirconium, aluminium, beryllium, chromium, uranium and also alkaline earth metals if interfering acids are present. It should be noted that a solution containing a thallic salt gives a black precipitate with ammonium sulphide. The precipitate is partly dissolved by cold dilute acid leaving a brownish residue which forms part of the copper group. The detailed analysis of the precipitate is given in Part B of this paper.

Procedure VI

The filtrate from *Procedure V* which now contains the metals of the iron and aluminium groups as well as cerium and thorium is treated as usual with excess of caustic soda, sodium peroxide, and sodium carbonate, boiled to decompose excess of sodium peroxide and filtered. The precipitate will contain the hydroxides of manganese, thallium, iron, titanium, zirconium (Iron group), cerium and thorium, as well as alkaline earth metals if interfering acids are present. The filtrate contains all the metals of the aluminium group except vanadium, *viz.*, chromium, uranium, zinc, beryllium and aluminium and is analysed by a method given in Part B.

Procedure VII

The precipitate obtained in *Procedure VI* is dissolved in the minimum quantity of concentrated hydrochloric acid the solution is diluted so that the concentration of acid is about $0.5N$ (test with methyl violet solution) and treated with excess of saturated oxalic acid solution. Any precipitate of oxalates formed is filtered off and tested for cerium and thorium as given in Part B. The filtrate is analysed for metals of the iron group by a method given in Part B.

The separation of metals into different groups according to the new scheme may be represented diagrammatically as follows:-

Solution containing all the basic radicals
Treat with concentrated $(NH_4)_2S$ reagent and filter

- Fil.
  Containing thiosalts alkaline earth metals and alkalis
  Boil with conc. HCl and filter
  - Ppt
    Sulphides of As, Se, Te, Mo, Pt, Au, and V.
  - Fil.
    Chlorides of Sb, Sn, (V) Alkaline earth metals and alkalis
    Treat with H_2O_2 and and $(NH_4)_2S$, acidify with dil. HCl and filter
    - Ppt
      Sulphides of Sb,Sn and (V)
    - Fil.
      Chlorides of alkaline earth metals and alkalis
- Ppt
  containing hydroxides and sulphides
  Treat with cold dil. (1*N*) HCl and filter
  - Fil.
    Chlorides of Ce, Th, Iron group, Aluminium group and alkaline earth metals if interfering acids are present.
    Treat with NaOH, Na_2O_2 and Na_2CO_3 Boil and filter
    - Ppt
      Iron group (Mn,Fe,Ti,Zr, and Tl) Ce and Th
      Dissolve in conc. HCl, dilute and treat with excess oxalic acid
      - Ppt
        Oxalates of Ce and Th
      - Fil.
        Mn,Fe, Ti, Zr,(Tl) and alkaline earth metals
    - Fil.
      Aluminium group (Al,Be,U,Zn,Cr)
  - Ppt
    Sulphides of Hg,Pb,Bi, Cu,Cd,Ni,Co, and Tl

SUMMARY

1. A new scheme of qualitative analysis for mixtures containing the common as well as the so-called "rare" elements has been discussed.

2. The new scheme is based upon the immediate formation of thiosalts by metals of the arsenic group (and vanadium) on adding concentrated ammonium sulphide solution and the subsequent decomposition of the thiosalts with excess of hydrochloric acid.

3. This scheme has the following advantages over the classical scheme now in use:

References p. 215.

a. The slow precipitation of the copper and arsenic groups by hydrogen sulphide in hydrochloric acid solution has been replaced by a more simple and rapid method of precipitating the sulphides completely. A considerable saving of time taken in analysis is thus effected.

b. The use of the hydrogen sulphide gas which is extremely inconvenient especially in large classes of students, has been eliminated and its place has been taken by concentrated ammonium sulphide—a reagent which can be easily prepared and used as a shelf reagent.

c. The use of yellow ammonium sulphide which does not give a satisfactory separation of the copper group from the arsenic group has been eliminated.

d. As the main features of the new scheme are similar to those of the classical scheme the student who has been trained in the old technique can take to the new scheme without much difficulty.

RÉSUMÉ

1. Un nouveau procédé d'analyse qualitative d'éléments courants et d'éléments rares est discuté.

2. Ce nouveau procédé est basé sur la formation immédiate de thiosels des métaux du groupe de l'arsenic (et vanadium) par addition d'une solution concentrée de sulfure d'ammonium, et sur la décomposition des thiosels formés par l'acide chlorhydrique.

3. Ce schéma d'analyse présente les avantages suivants sur la méthode classique utilisée actuellement:

a. La précipitation lente des éléments des groupes du cuivre et de l'arsenic par l'hydrogène sulfuré en solution chlorhydrique est remplacée par une méthode plus simple et plus rapide, permettant de précipiter quantitativement les sulfures (gain de temps considérable).

b. L'emploi d'hydrogène sulfuré, extrêmement désagréable (tout spécialement dans les laboratoires fréquentés par de nombreux étudiants) est supprimé et remplacé par le sulfure d'ammonium, en solution concentrée (se préparant facilement et utilisé comme un simple réactif).

c. Le sulfure d'ammonium jaune ne doit pas être utilisé pour la séparation des éléments du groupe du cuivre et du groupe de l'arsenic, il ne permet pas une séparation satisfaisante.

d. Les réactions de cette nouvelle méthode sont semblables à celles de l'analyse classique; les étudiants n'auront pas de peine à passer de l'une à l'autre.

ZUSAMMENFASSUNG

1. Es wurde ein neues qualitatives Analysenschema für Mischungen, die sowohl die gewöhnlichen, wie die sogn. „seltenen" Elemente enthalten, besprochen.

2. Das neue Schema gründet sich auf die sofortige Bildung der Thiosalze von Metallen der Arsengruppe (und Vanadium) beim Hinzufügen von konz. Ammonsulfidlösung und darauffolgender Zersetzung der Thiosalze mit einem Überschuss von Salzsäure.

3. Dieses Schema hat die folgenden Vorteile vor dem nun gebräuchlichen klassischen Schema:

a. Die langsame Ausfällung der Kupfer- und Arsengruppe mit Schwefelwasserstoff in salzsaurer Lösung wurde durch eine einfachere und raschere Methode der vollständigen Ausfällung der Sulfide ersetzt. Eine beträchtliche Zeiteinsparung bei der Analyse wird so erreicht.

b. Der Gebrauch der besonders bei einer grossen Anzahl Studenten äusserst unbequemen Schwefelwasserstoffgases wurde abgeschafft und es wurde durch das

konz. Ammoniumsulfidreagenz ersetzt, das leicht dargestellt und als Standreagenz benutzt werden kann.

c. Der Gebrauch des gelben Ammoniumsulfids, das keine befriedigende Trennung der Kupfergruppe von der Arsengruppe gewährt, wurde abgeschafft.

d. Da die Hauptzüge des neuen Schemas dem des klassischen Schemas ähnlich sind, können die Studenten, die nach der alten Methode gearbeitet haben ohne viel Schwierigkeit zu dem neuen Schema übergehen.

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THE APPLICATION OF THIOSALTS IN ANALYSIS

III. A NEW SCHEME OF QUALITATIVE ANALYSIS — Part B

by

I. K. TAIMNI AND R. P. AGARWAL

Chemical Laboratories, University of Allahabad, Allahabad (India)

In a previous paper[1] it was shown that in the qualitative analysis of a mixture the basic radicals can be divided into separate groups on the basis of the formation and subsequent decomposition of thiosalts. In this paper it is proposed to give the necessary details of the procedure which has to be adopted in detecting the metals belonging to different groups.

As some of the groups of basic radicals in the new scheme contain practically the same metals as those in the well-known scheme of NOYES, BRAY AND SPEAR[2], we have given only the bare outlines of the procedure adopted in the detailed analysis of such groups and the student can refer to the above paper for fuller details. Where a group contains a new combination of metals or a simpler procedure is recommended by us for its detailed analysis necessary details are given. Although organic reagents are of great use in the separation and detection of metals in the different groups we have avoided, as far as possible, tests based on the use of such reagents, so that the scheme may remain as simple as possible.

Analysis of the arsenic group

(Precipitate obtained in Procedure III)

The precipitate may contain As_2S_5, PtS_2, Au_2S_3, SeS_2 (Se), TeS_2 (Te), MoS_3 and V_2S_5. The precipitate is boiled with aqua regia, the solution evaporated and crystallized with KCl.

Ppt: K_2PtCl_6	Fil.: H_3AsO_4, $AuCl_3.2H_2O$, H_2SeO_3, H_2TeO_3, H_2MoO_4, H_3VO_4 Make alkaline with NaOH, treat with magnesia mixture and filter.

Ppt: $MgNH_4AsO_4$	Fil.: $NaAuO_2$, Na_2SeO_3, Na_2TeO_3, Na_2MoO_4, Na_3VO_4 Reduce with oxalic acid, digest on water bath and filter.

Ppt: Au	Fil.: H_2SeO_3, H_2TeO_3, H_2MoO_4, H_3VO_4, Reduce with Na_2SO_3 in presence of $7N$ cold HCl. Filter.

Ppt: Se	Fil.: H_2TeO_3, H_2MoO_4, H_3VO_4 Reduce the solution with Na_2SO_3 in dil. HCl solution containing KI and filter.

Ppt: Te	Fil.: H_2MoO_4, H_3VO_4, Divide the solution in two parts

(1)	(2)
Add KCNS and Zn Red solution Mo	Add H_2O_2 drop by drop, Orange red colour shows V (Mo gives only a yellow colour)

Note on the behaviour of tungstic acid

Any tungstate present alone in the mixture will be converted into insoluble tungstic oxide on treatment with concentrated nitric acid and concentrated hydrochloric acid in Procedure I. If tungstate is present together with phosphate or silicate, most of it will be converted into insoluble tungstic oxide as usual. The very small portion that may pass into solution along with other soluble substances is converted into thiotungstate on treatment with concentrated ammonium sulphide solution in Procedure II. On boiling this solution with $6N$ hydrochloric acid (Procedure III) the thiotungstate is partly decomposed giving a precipitate of tungstic sulphide which forms part of the arsenic group, while the remaining portion passes into the filtrate along with antimony and tin. The precipitate of tungstic sulphide in the arsenic group is converted into insoluble tungstic oxide on treatment with aqua regia for the solution of sulphides of the arsenic group and can be filtered off and tested for tungsten as usual. The solution containing the undecomposed thiotungstate along with antimony and tin, is evaporated to dryness with concentrated nitric acid, the residue taken up with dilute hydrochloric acid and the insoluble tungstic oxide filtered off. The filtrate is then treated as usual with concentrated ammonium sulphide (Procedure IV). Even in the presence of phosphate and silicate, the amount of tungstate which passes into solution after treatment with concentrated nitric acid and concentrated hydrochloric acid is very small. The detection of tungsten is therefore not included in the detailed analyses of the arsenic group.

Analysis of solution containing Sb, Sn, V, alkaline earth metals and alkalis

(Filtrate obtained in Procedure III)

The solution may contain the chlorides of Sb, Sn, V, Ca, Sr, Ba, Mg, Na, K and Li. Boil off H_2S, add excess of H_2O_2 to oxidize V to pervanadate, and then conc. $(NH_4)_2S$ reagent in excess. The solution containing thiosalts of Sn, Sb and V is treated with excess of dil. HCl and filtered (Procedure IV).

Ppt:	SnS_2, Sb_2S_3, V_2S_5 Boil with 6*N* HCl and filter.	Fil.:	Chlorides of Ca, Sr, Ba, Mg, Li, Na and K. Add excess of NH_4OH, conc. $(NH_4)_2CO_3$ and alcohol. Filter after ½ hour.

Ppt:	V_2S_5 Dissolve in HNO_3 add H_2O_2 orange red colour shows V	Fil.:	Chlorides of Sn,Sb Treat solution with clean iron wire, heat for 5 minutes and filter.	Ppt:	$CaCO_3$, $BaCO_3$ $SrCO_3$, $MgCO_3$, $(NH_4)_2CO_3$ Treat as usual.	Fil.:	Carbonates of Li, Na, and K. Treat as usual.

Ppt: Sb Dissolve in HNO_3 and test for Sb by adding $(NH_4)_2S$ and HCl orange coloured Ppt. shows Sb	Fil: $SnCl_2$ Add $HgCl_2$, White Ppt turning grey shows Sn

Analysis of copper group

(Precipitate obtained in Procedure V)

The precipitate may contain sulphides of Hg, Pb, Bi, Cu, Cd, Ni, Co and a part of Tl. Boil with 1 : 2 HNO_3 and filter.

Ppt: HgS	Fil.:	Nitrates of Pb, Bi, Cu, Cd, Ni, Co, and Tl. Evaporate to fumes with conc. H_2SO_4, dilute and filter.

Ppt: $PbSO_4$	Fil.:	Sulphates of Bi, Cu, Cd, Ni, Co, and Tl. Add H_2SO_3 to reduce thallium and then excess of NH_4OH. Filter.

References p. 222.

Ppt: $Bi(OH)_3$

Fil.: Ammonia complexes of Cu, Cd, Ni and Co and TlOH. Acidify with dil. HCl, boil off SO_2, add bromine water to reoxidize thallous to thallic salt, boil off excess of bromine. Add NH_4OH in excess . Filter.

Ppt: $Tl(OH)_3$

Fil.: Ammonia complexes of Cu, Cd, Ni and Co. Acidify with HCl and boil with $Na_2S_2O_3$. Filter.

Ppt: CuS

Fil.: Chlorides of Cd, Ni and Co, boil off SO_2 completely, add $(NH_4)_2CO_3$ in excess and filter.

Ppt: $CdCO_3$

Fil.: Ammonia complexes of Ni and Co. Add acetic acid in excess and KNO_2, filter after 10 minutes.

Ppt:	Fil.:
$K_3Co(NO_2)_6$ Test with borax bead. Blue bead shows	$Ni(CH_3COO)_2$ Add $(NH_4)_2S$ in excess. Black ppt of NiS shows
Co	Ni

Note: As the solution containing all the basic radicals is treated with concentrated ammonium sulphide in Procedure II there is the possibility of the precipitation of insoluble thiosalts with the free basic radicals present in the solution. A systematic study of the reactions of thiosalts with different metals in solution was undertaken and it was found that an insoluble compound is formed only in one case. When a solution containing thioselenite is treated with a thallous or thallic salt a black precipitate is obtained and the precipitate contains all the selenium if sufficient thallium is present in the solution. The exact composition of this black compound has not been determined but the modification which has to be introduced in the analysis of the copper group owing to the presence of this compound has been worked out. When both selenium and thallium are present in the original mixture, selenium, as shown above, goes with the precipitate obtained with ammonium sulphide (Procedure II). As the black precipitate is insoluble in cold 1*N* hydrochloric acid it forms part of the copper group and is found associated with copper, mercury, etc. On treatment with 1 : 2 nitric acid thallium in the black precipitate goes into solution while selenium is left undissolved along with HgS. On treatment of the insoluble residue with aqua regia both HgS and Se dissolve and selenium can be detected in the solution by reduction with sodium sulphite. After selenium has been filtered off mercury can be detected in the filtrate as usual with $SnCl_2$.

Analysis of aluminium group

(Filtrate obtained in Procedure VI)

The solution may contains Na_2CrO_4, Na_2UO_5, Na_2ZnO_2, $NaAlO_2$ and Na_2BeO_2. Boil to decompose Na_2O_2 completely, cool, acidify with dil. HNO_3 and add excess of NH_4OH. Filter.

Ppt: $Al(OH)_3$, $Be(OH)_2$, $(NH_4)_2U_2O_7$ Dissolve in dil. HCl, add excess of NaOH and filter.	Fil.: $(NH_4)_2CrO_4$, $Zn(NH_3)_6(OH)_2$ Acidify with acetic acid and add $BaCl_2$. Filter.

Ppt: $Na_2U_2O_7$ Dissolve in acetic acid, add NH_4NO_3 and sodium phosphate. White ppt of $UO_2NH_4PO_4$ confirm by $K_4Fe(CN)_6$ test.	Fil.: $NaAlO_2$, Na_2BeO_2 Dissolve in dil. HCl add solid $(NH_4)_2CO_3$ in large excess in cold. Filter after 10 min.	Ppt: $BaCrO_4$	Fil.: $Zn(CH_3COO)_2$ Add $(NH_4)_2S$ in excess. A white ppt of ZnS shows Zn.

Ppt: $Al(OH)_3$ Test by $Co(NO_3)_2$ test.	Fil.: Complex Be Carbonate. Boil until $(NH_4)_2CO_3$ is completely decomposed. Ppt of $Be(OH)_2$ shows Be. Confirm by $Co(NO_3)_2$ test.

Analysis of iron group

(Filtrate obtained in Procedure VII)

The filtrate may contain the chlorides and oxalates of Mn, Fe, Ti, Zr and Tl, as well as alkaline earth metals if an interfering acid was present in the original mixture. Evaporate the solution to dryness with conc.HNO_3 to remove HCl. Boil the residue with conc. HNO_3 and $KClO_3$ to decompose oxalic acid and precipitate Mn. Filter through asbestos.

Ppt: MnO_2	Fil.: Nitrates of Fe, Ti, Zr and Tl and alkaline earth metals. Test for phosphate. If present test for iron in a small portion and eliminate phosphate from the remaining solution as $FePO_4$ by adding $FeCl_3$ to acetate solution. Boil and filter hot. If phosphate is absent add NH_4OH in excess and filter. As Zr and Ti are not quite completely precipitated in the procedure for elimination of phosphate the filtrate after elimination of phosphate is treated with excess of NH_4OH, boiled and filtered for complete precipitation of these two elements.

Ppt: Basic acetates, hydroxides, or phosphates of Fe, Ti, Zr, Tl. Dissolve precipitate in the minimum quantity of 5*N* H_2SO_4, add half the volume of 5*N* acid in excess. Filter if solution is not quite clear. Test portions of solution as follows:—	Fil: Acetates of alkaline earth metals. Combine with filtrate from proc. IV

(1)	(2)	(3)
To a portion of solution add KI and Na_2SO_3 TlI. Yellow precipitate shows presence of Tl.	To another portion of solution add KCNS solution. $Fe(CNS)_3$. Blood red colour shows presence of Fe.	To the remaining portion add H_2O_2 in excess. A yellow to orange colour indicates presence of Ti. If Fe is present the solution should be sufficiently diluted with water before adding H_2O_2. To the solution which has been tested for Ti add Na_2HPO_4, and heat to 70°-80° C. Keep aside for 10 minutes. A white ppt of $Zr(OH)PO_4$, shows presence of Zr.

Detection of cerium and thorium

(Precipitate obtained in Procedure VII)

The precipitate may contain $Ce_2(C_2O_4)_3$ and $Th(C_2O_4)_2$. Boil precipitate with conc. HNO_3 and $KClO_3$ to decompose oxalate and evaporate to dryness. Dissolve neutral residue in water. Divide in two parts:-

(1)	(2)
Test one portion for Ce by either of the two following methods:— (1) Boil with conc. HNO_3 and PbO_2. A yellow colour in supernatant liquid shows presence of Ce (2) Add NH_4OH and H_2O_2. Orange coloured precipitate shows presence of Ce	Test the remaining solution for thorium by boiling the neutral solution with $Na_2S_2O_3$. A white precipitate of $Th(OH)_4$ shows presence of Th

References p. 222.

SUMMARY

The detailed analysis of the various groups according to the new scheme given in the previous paper has been given.

RÉSUMÉ

Les détails de l'analyse de différents groupes d'après la nouvelle méthode proposée dans les mémoires précédents sont donnés.

ZUSAMMENFASSUNG

Die eingehende Analyse der verschiedenen Gruppen nach dem in früheren Arbeiten benutzten neuen Schema wurde gegeben.

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REMOVAL OF PHOSPHATE ION BY ION-EXCHANGE

by

RICHARD B. HAHN, CHARLOTTE BACKER AND ROY BACKER

Chemistry Department, Wayne University, Detroit 1, Michigan (U.S.A.)

DISCUSSION

One very troublesome ion encountered in the ordinary qualitative analysis scheme is the phosphate ion which interferes in the analysis of the ions precipitated by hydrogen sulfide in ammoniacal solution and those precipitated as carbonates (Cr^{+3}, Fe^{+3}, Al^{+3}, Co^{+2}, Ni^{+2}, Zn^{+2}, Mn^{+2}, Ba^{+2}, Ca^{+2} and Sr^{+2}). Various chemical methods for the removal of phosphate ion have been proposed[3] but these all have the disadvantage that an additional cation is introduced in the process, which also must be eliminated. This difficulty can be overcome by the use of an ion-exchange resin. The use of ion-exchange resins in analytical chemistry for the removal of interfering ions has been the subject of many investigations. Many methods of analysis have been simplified through their use. SAMUELSON[5] has shown in the determination of alkali metals in the presence of phosphate that the interference can be eliminated by passing the solution through a sulfonic acid exchanger, and eluting with an ammonium chloride solution. This procedure is more rapid and less subject to error than a phosphate precipitation, but the elution of the alkali metals is also subject to serious error.

Using this same principle, HELRICK AND RIEMAN[1] devised a rapid, accurate method for the determination of phosphorus in phosphate rock using a cation exchanger. The cations were removed by the resin, the phosphorus was determined in the effluent, and the cations were removed from the resin by regeneration with a solution of hydrochloric acid. Attempts have been made to remove the phosphate ion with weakly basic resins[2]. The results have not been successful since these resins absorb the monovalent ions more strongly than the polyvalent ions.

Recently a strongly basic anion exchanger, "Amberlite IRA-400", has become available. This resin is a modified amine polymer which is supplied in the chloride form. Unlike the weakly basic anion exchange resins, this strongly basic resin has the greatest affinity for polyvalent ions. The relative affinity of Amberlite IRA-400 for various anions is given[7]:

$$PO_4^{-3} > SO_4^{-2} > Cl^- > OH^-$$

Because of this property, Amberlite IRA-400 was investigated as a means to remove the phosphate ion.

EXPERIMENTAL

Preparation of the column and the resin

The column used was the experimental type described by TOMPKINS, KHYM AND COHN[4,6]. The column was about 1 cm in diameter. Enough Amberlite IRA-400 resin was added to give a bed of about 20 cm in depth (about 30 g of resin). This type of column has the advantage that it cannot run dry; however, a 50 ml burette may be used as a column if it is watched constantly.

The resin was prepared by treating it with a saturated solution of sodium chloride then washing two to three times with distilled water. The column and resin prepared in this manner was used throughout the entire investigation. After use, the resin can be regenerated by the same process.

Removal of the phosphate ion

The capacity of the column was tested by passing through varying amounts of sodium dihydrogen phosphate solution and/or phosphoric acid solution. It was found that the phosphate ion was removed in amounts up to 300 mg.

The effect of various cations upon the removal of the phosphate ion was studied. Twenty milligrams of the ions of groups III and IV (Cr^{+3}, Al^{+3}, Fe^{+3}, Mn^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Ca^{+2}, Ba^{+2} and Sr^{+2}) each individually along with twenty milligrams of the phosphate ion in a solution 0.25*N* in hydrochloric acid were passed through the column. The effluents were analyzed for the phosphate ion and the cation. In each case the phosphate ion was completely removed and the original amount of the cation was found in the effluent. Mixtures of all the ions of groups III and IV with the phosphate ion were also tested. The phosphate ion was removed completely from these mixtures without affecting the quantity of the cations.

A final test was made by mixing together 20 mg each of the ions of groups II, III and IV along with 100 mg of the phosphate ion. The acidity was adjusted to 0.25*N* in hydrochloric acid and the group II ions precipitated with hydrogen sulfide. The filtrate was passed through the exchange column then analyzed for the phosphate ions and the ions of group III and IV. As in the previous cases, the phosphate ion was removed completely while the cations passed through the column unaffected.

Removal of the phosphate ion by using the resin in a batch process was also studied. In this case, about 2 g of the resin was stirred up with the phosphate containing solution. Although part of the phosphate ion was removed by this method, a complete removal was never attained. Hence the use of a column is essential.

CONCLUSION

These experiments show that the phosphate ion can be removed rapidly and easily by the use of a strongly basic ion-exchange resin, Amberlite IRA-400. The method is more rapid than chemical methods and no foreign cations are introduced in the removal.

SUMMARY

A method for the removal of the phosphate ion is described. This is accomplished by the use of an anion exchanger, Amberlite IRA-400. The method is rapid and no foreign cations are introduced in the process.

RÉSUMÉ

On décrit une méthode pour la séparation de l'ion phosphorique. La séparation s'accomplit à l'aide de l'échangeur d'ions ,,Amberlite IRA-400". La méthode est rapide et il n'y a pas introduction de cations étrangers au cours de la séparation.

ZUSAMMENFASSUNG

Eine Methode für die Entfernung des Phosphat-ions mit Hilfe des Ionenaustauschers Amberlite IRA-400 ist beschrieben. Die Methode arbeitet schnell und zeichnet sich dadurch aus, dass keine fremden Kationen in dem Prozess eingeführt werden.

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COLORATION OF MELTED POLYPHOSPHATES BY COBALT, NICKEL AND COPPER, AND AN EXPLANATION OF THE REACTIONS IN THE MICROCOSMIC SALT BEAD

by

MORITZ KOHN *

Chemical Laboratory of the University of Havana (Cuba)

It was observed by SAN MARTIN[1] some years ago that the microcosmic salt bead of cobalt which is reddish violet turns blue if a small quantity of Na_2CO_3 is added in the preparation of the bead. This change of the color was explained[2] by the formation of sodium pyrophosphate

$$Na_2CO_3 + 2NaPO_3 = Na_4P_2O_7 + CO_2.$$

However, it was found that potassium sodium pyrophosphate[3], if it is melted after addition of $CoCl_2$, yields a blue porcellaneous melt while the microcosmic salt bead of cobalt is glassy and contains an excess of sodium metaphosphate**. But it must be considered that FLEITMANN AND HENNEBERG[4], SCHWARZ[5] and later STANGE[6] had reported that pyrophosphate reacts with metaphosphate forming polyphosphates, for instance, sodium tetraphosphate ($Na_6P_4O_{13}$) in the reaction of 1 mol $Na_4P_2O_7$ with 2 mol $NaPO_3$

$$Na_4P_2O_7 + 2\ NaPO_3 = Na_6P_4O_{13}$$

Therefore, it must be concluded that the blue microcosmic salt bead of cobalt prepared after addition of Na_2CO_3 contains cobalt sodium polyphosphates.

Cobalt. I. 3 g $NaH_2PO_4 + H_2O$ were mixed with 3 ml 0.1 *M* $CoCl_2$ in a porcelain crucible. The water was evaporated; the dry mass was melted until no further change could be observed. When the crucible cooled down it contained a glassy reddish violet substance.

II. The reaction was carried out with the same quantities as in I, but 0.2 g Na_2CO_3 were added. The mixture had to be melted until the generation of CO_2 stopped. When the crucible cooled down it contained a glassy substance which was more blue than in I. 5 ml water were added to the substances in the two crucibles which were kept at room temperature for 24 hours. After this time the contents of the crucibles were stirred whereby syrupy solutions resulted. The solution in II was darker blue than the solution in I. This could also be observed if the contents of the crucibles were poured into test tubes.

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* Present address: 536 West 113th Street, New York 25, N.Y.

** By sodium metaphosphate sodium hexametaphosphate $(NaPO_3)_6$ is always meant here.

Nickel. The reactions were carried out with the same quantities as in the case of cobalt. The glassy mass prepared after addition of Na_2CO_3 was more yellowish brown than in the experiment without Na_2CO_3.

Copper. The experiments were carried out in the same way as explained above. The glassy substance prepared after addition of Na_2CO_3 was more blue than the greenish blue substance prepared without Na_2CO_3. The water solution in the former case was more blue than the greenish blue water solution prepared in the later case.

A glassy substance prepared by melting a mixture of 3 g $NaH_2PO_4 + H_2O$ and 0.2 g Na_2CO_3 should be a sodium polyphosphate containing about 13 phosphorus atoms.

Sodium hexametaphosphate melted after addition of $CuSO_4$ can only yield a glassy mass containing copper sodium hexametaphosphate. This reaction will take place in the preparation of the microcosmic salt bead if a metallic salt is used (for instance $CuSO_4$), which can not be decomposed under these conditions to a metallic oxide.

But if, instead of $CuSO_4$, CuO is used, another course of reactions was to be expected.

I. 3.1 g $NaH_2PO_4 + H_2O$ and 4 ml 0.1*M* $CuSO_4$ if melted after the removal of the water give a greenish blue glassy mass.

II. 3.1 g $NaH_2PO_4 + H_2O$ and a quantity of CuO equivalent to 4 ml 0.1 molar $CuSO_4$ *i.e.* 0.0320 g CuO were melted. The crucible contained a glassy mass which was obviously more blue than in I.

III. 3.1 g sodium tetraphosphate ($Na_6P_4O_{13}$) (manufactured in U.S.A. by Rumford Chemical Works, Rumford, L.I. N.Y.) was mixed with 4 ml 0.1*M* $CuSO_4$. Water was evaporated and the residue melted.

IV. 3.1 g sodium tetraphosphate melted after addition of 0.0317 g CuO (it is equivalent to 4 ml 0.1*M* $CuSO_4$) gave a clear blue glassy melt. The darkness of the color increased from experiment I to experiment IV.

If CuO is added to sodium metaphosphate, copper sodium orthophosphate will be obtained.

$$NaPO_3 + CuO = CuNaPO_4$$

This substance could add $NaPO_3$ forming copper sodium pyrophosphate $CuNaPO_4 + NaPO_3 = CuNa_2P_2O_7$ and the pyrophosphate could add again x molecules of sodium metaphosphate forming copper sodium polyphosphates:

$$CuNa_2P_2O_7 + x\,NaPO_3 = CuNa_{2+x}P_{2+x}O_{7+3x}$$

These reactions will take place in the preparation of the microcosmic salt bead if a metallic oxide (*e.g.* CuO) is used.

References p. 228.

ACKNOWLEDGEMENTS

The author wants to express his sincere thanks to the Head of the Department of Mineralogy of the University of Havana, Professor Dr R. SAN MARTIN, whose observations on the microscopic salt bead of cobalt prompted these investigations and to the Professors of Chemistry, Dr CARRERA AND Dr VARGAS, who gave the permission to work in the Chemical Laboratory of the University of Havana.

SUMMARY

The color of melted sodium hexametaphosphate that contains cobalt, nickel or copper, becomes darker if a small quantity of Na_2CO_3 is added in the preparation of the melt.

This change of color is explained by the formation of polyphosphates.

If in the preparation of the microcosmic salt bead metallic oxides are used the bead contains metallic sodium polyphosphates. But if metallic salts are used the bead contains metallic sodium hexametaphosphates.

RÉSUMÉ

La coloration de l'hexamétaphosphate de sodium fondu renfermant du cobalt, du nickel ou du cuivre, fonce par addition d'une petite quantité de CO_3Na_2.

Ce changement de coloration s'explique par la formation de polyphosphates.

Dans la préparation du sel microcosmique, si on utilise des oxydes métalliques, les perles obtenues contiennent des polyphosphates de sodium et si l'on utilise des sels métalliques, des hexamétaphosphates.

ZUSAMMENFASSUNG

Die Farbe von geschmolzenem Natriumhexametaphosphat, welches Kobalt, Nickel oder Kupfer enthält, wird dünkler, wenn eine kleine Menge von Na_2CO_3 bei der Herstellung der Schmelze zugefügt wird.

Diese Änderung der Farbe wird durch Bildung von Polyphosphaten erklärt.

Wenn bei der Herstellung der Phosphorsalzperle Metalloxyde benützt werden, enthält die Perle Polyphosphate der betreffenden Metalle. Wenn aber Metallsalze benützt werden, enthält die Perle Hexametaphosphate der betreffenden Metalle.

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SOLUBILITY OF SILVER PYROPHOSPHATE IN ALKALI PYROPHOSPHATES

by

MORITZ KOHN*

Laboratory of inorganic chemical technology, Technical University of Vienna (Austria)

More than a hundred years ago SCHWARZENBERG[1] found that silver pyrophosphate is insoluble in pyrophosphates, and FLEITMANN AND HENNEBERG[2] reported at the same time that silver pyrophosphate is insoluble in an excess of sodium pyrophosphate. These statements are erroneous.

Solubility of silver pyrophosphate in a cold saturated solution of sodium pyrophosphate

I. Silver pyrophosphate prepared by precipitation of sodium pyrophosphate with a small excess of silver nitrate was filtered with suction and washed with water in order to remove the sodium nitrate and the excess of silver nitrate. Afterwards the silver pyrophosphate was washed with a cold saturated solution of sodium pyrophosphate, put in a glass stoppered bottle, and a saturated solution of sodium pyrophosphate and some powdered sodium pyrophosphate were added. The mixture was shaken some times. The solution (temperature 26° C) was filtered after two days and the filtrate (134 ml) precipitated with diluted hydrochloric acid. The AgCl was filtered, washed with water, dried at 100° C and weighed: 0.0398 g, corresponding to 0.0420 g $Ag_4P_2O_7$.

II. 5 ml 0.1N $AgNO_3$ were mixed with 132 ml of a cold saturated solution of $Na_4P_2O_7$ and some powdered $Na_4P_2O_7 + 10H_2O$ was added. The following procedure was the same as in I. The filtrate (116 ml) gave 0.0367 g AgCl corresponding to 0.0387 g $Ag_4P_2O_7$.

Therefore 100 ml of the solution I contained 0.03134 g,
100 ml of the solution II 0.03335 g $Ag_4P_2O_7$.

Solubility of silver pyrophosphate in potassium pyrophosphate

Powdered K_2HPO_4 was heated in a crucible the bottom of which was kept glowing for about half an hour. Afterwards the flame was removed. When the crucible had cooled down, the white cake was taken out and triturated in a mortar. The powdered substance was heated again in the crucible and stirred with a spatula in order to prepare a homogeneous substance. The reaction is complete if a sample dissolved in water after the addition of $AgNO_3$ gives a pure white precipitate of $Ag_4P_2O_7$. A yellowish tinge indicates the presence of Ag_3PO_4. In this case the substance has to be powdered and heated again. Since a solution of $Na_4P_2O_7 + 10H_2O$ saturated at 0° C contains 5.4 g, an equimolecular solution of $K_4P_2O_7$ should contain 3.99 g.

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* Present address: 536 West 113th Street, New York 25, N.Y.

I. 6.75 g $K_4P_2O_7$ were dissolved in water to a volume of 150 ml. $Ag_4P_2O_7$ was washed with 15 ml of this solution and afterwards put in the residue *i.e,* 135 ml of this solution. The solubility was determined as explained above. 126 ml of the filtrate gave 0.0954 g AgCl corresponding to 0.1007 g $Ag_4P_2O_7$. Therefore 100 ml of this solution contained 0.0798 g $Ag_4P_2O_7$.

II. 139 ml of a solution of 6.75 g $K_4P_2O_7$ in water were added to 11 ml 0.1N $AgNO_3$. The turbid mixture was shaken and filtered after 24 hours. 140 ml of the filtrate gave 0.1098 g AgCl; this corresponds to 0.1159 g $Ag_4P_2O_7$. Therefore 100 ml of this solution contained 0.0827 g $Ag_4P_2O_7$.

The experiments I and II show that a solution of $K_4P_2O_7$ equimolecular to a cold saturated solution of sodium pyrophosphate dissolves about double the quantity of $Ag_4P_2O_7$.

III. A solution of 8 g $K_4P_2O_7$ in 200 ml water was prepared. $Ag_4P_2O_7$ washed with this solution in a glass sinter crucible was added to the residue of this solution and the mixture, which was shaken sometimes, was kept two days in a bottle. After this time the mixture was filtered. 150 ml of this filtrate gave 0.1204 g AgCl; this corresponds to 0.1081 g $Ag_4P_2O_7$. Therefore 100 ml of this solution contain 0.0720 g $Ag_4P_2O_7$.

IV. A solution of 16.5 g $K_4P_2O_7$ in 100 ml water was prepared. The addition of 21.6 ml 0.1N $AgNO_3$ was necessary to produce a slight turbid mixture. Therefore 121.6 ml contained 0.3270 g $Ag_4P_2O_7$ and 100 ml contained 0.2687 g $Ag_4P_2O_7$.

V. A solution of 8.25 g $K_4P_2O_7$ in 100 ml water was prepared. 8.28 ml 0.1M $AgNO_3$ were added to obtain a slight turbid mixture. Therefore 108.28 ml of this mixture contained 0.1253 g $Ag_4P_2O_7$ and 100 ml 0.1157 g $Ag_4P_2O_7$.

VI. To 5.9 g $K_4P_2O_7$ and 0.6 g $Ag_4P_2O_7$ water was added to a volume of 15 ml. The mixture was shaken and filtered with suction through a glass sinter crucible. 13 ml of this filtrate were diluted with water to 75 ml and precipitated with diluted HCl, whereby 0.2158 g AgCl resulted, corresponding to 0.2278 g $Ag_4P_2O_7$. Therefore 100 ml of this solution contained 1.75 g $Ag_4P_2O_7$.

The experiments I-VI were carried out at a temperature of 29° C. The results of the experiments are sufficient to show that the solubility of $Ag_4P_2O_7$ increases with the increasing concentration of the potassium pyrophosphate.

References p. 231.

SUMMARY

Silver pyrophosphate is, according to the observations of former investigators, insoluble in alkali pyrophosphates. These statements are erroneous. 100 ml of a cold saturated solution of sodium pyrophosphate dissolve about 0.0324 g $Ag_4P_2O_7$. Silver pyrophosphate is much more soluble in potassium pyrophosphate and the solubility increases with the increasing concentration of the potassium pyrophosphate.

RÉSUMÉ

Le pyrophosphate d'argent est, d'après certains auteurs, insoluble dans les pyrophosphates alcalins. Ces constatations sont fausses. 100 ml de solution saturée froide de pyrophosphate de sodium dissolvent environ 0.0324 g de $Ag_4P_2O_7$. Dans le pyrophosphate de potassium, le pyrophosphate d'argent est encore beaucoup plus soluble, et la solubilité augmente avec l'augmentation de concentration du pyrophosphate de potassium.

ZUSAMMENFASSUNG

Silberpyrophosphat ist gemäss den Beobachtungen früherer Autoren unlöslich in Alkalipyrophosphaten. Diese Feststellungen sind irrig. Denn 100 ml einer kaltgesättigten Lösung von Natriumpyrophosphat lösen ungefähr 0.0324 g $Ag_4P_2O_7$. In Kaliumpyrophosphat ist Silberpyrophosphat viel mehr löslich und die Löslichkeit nimmt mit der steigenden Konzentration des Kaliumpyrophosphats zu.

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ON THE VOLUMETRIC DETERMINATION OF SILVER IN LEAD *

by

G. MANNELLI

Istituto di Chimica Analitica Università di Firenze (Italia)

The silver determination in lead is generally executed with the classical cupellation method, especially in industry.

We know, besides the above-mentioned method, other methods, which are based either on silver precipitation and subsequent gravimetric determination, or on physical methods (potentiometric, polarographic, electrolytic, colorimetric, spectrographic methods)[1].

The gravimetric method requires plenty of time for execution, while the physical methods often require apparatus which may not be available in all laboratories. The volumetric methods, which combine simplicity and a remarkable rapidity, have not been studied in this field.

WAGSTAFF[2] has proposed an indirect volumetric method based on silver precipitation with thiocyanate ions and subsequent titration of CNS^- ion with potassium permanganate. The values obtained are about 1.5% higher than those obtained by cupellation, and from data referred to by the author it is seen that the determination is possible up to a Ag:Pb ratio of the order of 1:3650.

FISHER, LEOPOLDI AND VON USLAR[3] have proposed the use of dithizone for volumetric measurements as well as colorimetric ones, which, according to the authors, allows the determination of amounts of silver between 120 and 0.5 γ even when it is present in lead in a ratio 10^{-5}: 1, for such very small amounts there is a 10% error approximately.

On account of its high sensitivity and its delicate technique, this method seems to be employable for the determination of silver traces rather than for a determination commonly required.

With the aim of contributing to the resolution of the problem of silver volumetric determination in lead with regard especially to the Ag:Pb relation, I have tried to see if such a determination is possible without separation of silver, avoiding every interference from lead.

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The difference of behaviour between lead and silver in respect to the ammonium salts of the tartaric and acetic acids, and the insolubility of the silver iodide in ammonia easily permit the separation of the two ions. VORTMANN AND HECKT[4] precipitate the silver iodide in the presence of ammonium tartrate. It is then heated at 130° until constant weight is obtained: nevertheless the two mentioned authors limit the ratio Ag:Pb to 1:12.

This determination may also be made quicker and applicable to the determination of very small amounts of silver even in the presence of considerable quantities of lead if the volumetric variation is rendered possible.

This is possible if we use an adsorption indicator in order to determine the end of Ag^+-ion precipitation.

After several experiments with the many indicators proposed for the silver iodometric determination, I have chosen bromphenol blue suggested by KOLTHOFF[5]. This indicator seems particularly useful because it also gives very good results in a slightly acid medium.

Either an ammonium tartrate or ammonium acetate solution may be employed; I have used the latter. With this method it is possible to determine quantities of silver of the order of 10^{-4} g up to till an Ag:Pb ratio 1:14,000. The solution, added to the indicator, at first assumes a violet colouring which at the equivalent point changes into purple. It may happen that the solution to be titrated may be slightly acidic and in this case in the beginning we have a gray-purple colour which becomes green-gray and then returns to a gray-purple colour at the equivalent point.

	Ag				
Pb	present	found	△	Ag%	Ag:Pb
0.0984	$1.08 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	0.00	1.10	1:92
0.0984	$7.16 \cdot 10^{-4}$	$7.16 \cdot 10^{-4}$	0.00	$7.27 \cdot 10^{-1}$	1:137
0.9840	$7.16 \cdot 10^{-4}$	$7.16 \cdot 10^{-4}$	$2.60 \cdot 10^{-5}$	$7.27 \cdot 10^{-2}$	1:1375
1.9680	$7.16 \cdot 10^{-4}$	$7.04 \cdot 10^{-4}$	$1.20 \cdot 10^{-5}$	$3.64 \cdot 10^{-2}$	1:2750
2.0100	$4.31 \cdot 10^{-4}$	$4.13 \cdot 10^{-4}$	$1.80 \cdot 10^{-5}$	$2.14 \cdot 10^{-2}$	1:4665
4.1440	$7.16 \cdot 10^{-4}$	$7.16 \cdot 10^{-4}$	0.00	$1.72 \cdot 10^{-2}$	1:5788
2.0310	$2.85 \cdot 10^{-4}$	$2.85 \cdot 10^{-4}$	0.00	$1.40 \cdot 10^{-2}$	1:7126
6.2160	$7.16 \cdot 10^{-4}$	$6.76 \cdot 10^{-4}$	$4.00 \cdot 10^{-5}$	$1.15 \cdot 10^{-2}$	1:8662
4.1440	$4.31 \cdot 10^{-4}$	$4.13 \cdot 10^{-4}$	$1.80 \cdot 10^{-5}$	$1.04 \cdot 10^{-2}$	1:9839
6.2160	$4.31 \cdot 10^{-4}$	$4.13 \cdot 10^{-4}$	$1.80 \cdot 10^{-5}$	$6.93 \cdot 10^{-3}$	1:14420
10.3600	$7.16 \cdot 10^{-4}$	$6.76 \cdot 10^{-4}$	$4.00 \cdot 10^{-5}$	$6.91 \cdot 10^{-3}$	1:14470

PROCEDURE

Weigh out accurately 1 g of the finely divided lead (according to the quantity of silver presumed present) into 50 ml beaker and cover with a clock-glass. Add 2 ml of water followed by 6 ml of concentrated nitric acid. When the vigorous reaction is over, evaporate on a water-bath to dryness. Add a few ml of water, 2-5 ml of a 30% ammonium acetate solution and 2-3 drops of bromphenol blue 0.1% solution. Titrate with standard $0.02N$ potassium iodide solution, or more dilute according to convenience.

When silver has to be determined in a lead salt a suitable solution is made and then the procedure followed in the same way.

Reagents employed

Bromphenol blue sodium salt and its 0.1% solution in water.
Potassium iodide of Pfizer Co. twice recrystallized.
Silver nitrate from silver 1000‰.

SUMMARY

A volumetric method is proposed for the determination of silver in lead consisting of titrating with a potassium iodide solution in the presence of ammonium acetate, using bromphenol blue as an adsorption indicator.

RÉSUMÉ

L'auteur propose un dosage d'argent dans le plomb par titration directe au moyen d'une solution titrée d'iodure de potassium en présence d'acétate d'ammonium, et de bleu de bromophénol, comme indicateur d'adsorption.

ZUSAMMENFASSUNG

Es wird die volumetrische Bestimmung des Silbers in Blei durch direkte Titrierung mit Kaliumjodid in Anwesenheit von Ammoniumacetat studiert, mit Anwendung von Bromphenolblau als Adsorptionsindikator.

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THE TITRATION OF COMPLEXONE III WITH THORIUM NITRATE AT pH 2.8-4.3

by

K. TER HAAR AND J. BAZEN

Analytical Laboratory N.V. Philips' Gloeilampenfabrieken, Eindhoven (Netherlands)

INTRODUCTION

It is known that numerous metal ions form very strong complex-compounds with Complexone III (disodium salt of ethylenediaminetetra-acetic acid, versene) which for the first time were systematically studied by BIEDERMANN[1].

In this reaction generally a quantity of H^+ equivalent to the quantity of metal ions is released and by means of titration of H^+ it is possible to determine the quantity of metal ions.

Later on SCHWARZENBACH[3] described other titration methods in which the end point is determined with the aid of an indicator. These methods are based on the fact that at a certain pH the metal ion forms a compound with the indicator (eriochrome black T or murexid), of which the colour differs from that of the indicator.

During the titration first the free metal ions are complexed and at the end point the metal ions bound to the dye are also bound by Complexone, while the indicator is released at the same time. The colour change is sharp, *e.g.* from red into blue (with eriochrome black T) or from red into violet (with murexid).

The drawback of the indicators mentioned is that the application is restricted to the pH range 10-12.

Both BIEDERMANN's dissertation and our own researches have shown that several metals, *e.g.* Ni, Fe, Al and Bi, still form very strong complexes also at a lower pH.

The advantage of a lower pH is that now fewer elements form complexes, so that the selectivity of the Complexone is increased. It might be attempted to find specific indicators for those elements which react at pH 2-4. Another solution is to add a small excess of Complexone and back-titrate it with a solution of a metal salt reacting with Complexone and with a dye.

For the reactions

$$Me^{+n} + Y^{-4} \rightleftharpoons MeY^{n-4} \quad a)$$

and

$$Me + \text{dye} \rightleftharpoons \text{Me-dye} \quad b)$$

the requirement must be made that reaction b) has a less strong tendency to the right than reaction a) (for an exact treatment of the problem see ref. 6).

For the solution of this problem an $FeCl_3$-solution might be used, with which rhodanide, sulfosalicylic acid or "tiron"[2] might serve as indicators. We first tried this, but the colour change is still uncertain, owing to the unfavourable conditions of the reactions a) and b).

We got excellent results with the element thorium which forms a strong complex with Complexone III, as also appears from the tests by CABELL[3], thorium giving also a sensitive colour reaction with alizarin-S, a reaction which is also used for the titrimetric determination of F.

From further tests with thorium nitrate it appeared that in this element we had found a very sensitive reagent to back-titrate an excess of Complexone at pH 2.4-4.8.

As we mentioned already in the discussion about the lecture by CABELL[4], this principle was developed by us for an Ni, Al and Bi determination with Complexone and, moreover, the reaction is perhaps suitable for a determination of thorium.

In the practical application of this titration method the admissible pH range is mainly fixed by the reaction between thorium and alizarin-S; it appeared from experiments that at room temperature a pH of 2.4-3.6 is most suitable; at boiling temperature it is even possible to work at a pH 4.8*.

The colour change in the titration is clearest when the excess of Complexone is titrated with thorium nitrate; here the change goes from yellow to red, a change that can even be determined, using 0.005*M* solutions, by the addition of 0.01-0.02 ml in a volume of 30 ml.

At an increasing pH of the solution the colour change becomes somewhat different: at pH 2.8 the solution remains bright yellow, but at the end point it changes into red; at pH 3.5 already the solution becomes a little orange-yellow, especially in the presence of much thorium-Complexone, but at the end point there is a very sharp change into red. This phenomenon is pronounced at pH 4.8, so that even at boiling temperature a change from dark orange into red is obtained. For practical use we should like to fix the highest admissible pH at 4.3.

The colour change at the end point is reversible, so that it is possible to back-titrate with Complexone to bright yellow. In some cases heating until boiling temperature is desirable, in consequence of which the solution becomes bright yellow, as otherwise it always remains more or less orange coloured.

The reaction between Th^{+4} and Complexone III (Na_2H_2X) is represented schematically by the reaction

$$Th^{+4} + Na_2H_2X \rightleftharpoons ThX + 2H^+ + 2Na^+$$

So per Mol thorium 1 Mol Complexone is bound[3].

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* This was communicated to us in a letter on the subject from Mr. H. FLASCHKA, Graz.

References p. 240.

To keep the change in pH within certain limits during the titration a buffer solution is added; for this purpose we selected monochloracetic acid-sodium acetate and acetic acid-sodium acetate.

REAGENTS

The reagents are preferably dissolved in deionized water. All reagents c.p. quality.

Complexone III $0.05M$:
18.6 g disodium salt of ethylenediaminetetra-aceticacid is dissolved and diluted to 1000 ml.
Thorium nitrate $0.05M$:
27.6 g $Th(NO_3)_4.4H_2O$ is dissolved and diluted to 1000 ml.
Monochloracetic acid $2M$:
189 g $CH_2ClCOOH$ is dissolved and diluted to 1000 ml.
Sodium acetate $1M$:
136 g $CH_3COONa.3H_2O$ is dissolved and diluted to 1000 ml.
Acetic acid $2M$:
Alizarin-S indicator solution 0.1%:
100 mg alizarin-S is dissolved and diluted to 100 ml.

PROCEDURE

A certain quantity of Complexone-solution is transferred to a beaker of 250 ml capacity and diluted to about 100 ml.

If necessary the solution is neutralized on congo red paper with HCl $2N$ or ammonia $2N$.

Then 5 ml monochloracetic acid and 5-10 ml sodium acetate solution are added and, if necessary, the pH of the solution is checked (pH 2.8-3.5; for pH 3.5 10 ml sodium acetate solution must be taken).

Then 1.5 ml alizarin-S is added and the solution titrated with thorium nitrate until the colour changes to orange-red.

At pH 3.5 the change is somewhat different from that at pH 2.8: during the titration the solution becomes more or less orange, but at the end point there is a sharp change into red.

For the titration at pH 4.3 the solution is buffered with 10 ml acetic acid and 10 ml sodium acetate, heated until boiling point and titrated with thorium nitrate.

Proportion of the consumption Complexone-thorium nitrate

Different quantities of Complexone solution $0.05M$ were titrated at pH 2.8, 3.5, and 4.3 with a thorium nitrate solution according to the method described.

First a small quantity of Complexone was titrated until colour change, then Complexone solution was added and again titrated with thorium nitrate etc., until 5 readings had been obtained. From these readings the proportion Complexone: thorium nitrate, the average x and the standard deviation S were calculated. When calculating statistically, the differences between the averages and the standard deviations at the different pH did not produce a significant F and t, so that the reaction in the area 2.8-4.3 is independent of the pH.

TABLE I

TITRATION OF COMPLEXONE-THORIUM NITRATE

pH 2.8				pH 3.5			
ml Co	ml Th	Co : Th	$\triangle\cdot10^3$	ml Co	ml Th	Co : Th	$\triangle\cdot10^3$
5.14	5.10	1.007	—7	5.15	5.07	1.015	—2.2
9.87	9.72	1.015	+1	10.32	10.15	1.016	—1.2
19.46	19.17	1.014	0	20.40	20.04	1.017	—0.2
31.48	30.93	1.017	+3	29.55	28.96	1.020	+2.8
38.22	37.57	1.017	+3	37.58	36.87	1.018	+0.8
	$\bar{x}$ =	1.0140			$\bar{x}$ =	1.0172	

$$S^2 = \frac{(x_1 - \bar{x})^2}{n - 1} = 17\cdot10^{-3} \qquad S^2 = 3.7\cdot10^{-3}$$

100 ml volume	100 ml volume
5 ml mono-Cl-acetic acid 2*M*	5 ml mono-Cl-acetic acid 2*M*
5 ml Na-acetate 1*M*	10 ml Na-acetate 1*M*
1.5 ml al.-S ind. 0.1%	1.5 ml al.-S ind. 0.1%
pH 2.8 before titration	pH 3.5 before titration
pH 2.35 after titration	pH 2.9 after titration

pH 4.3

ml Co	ml Th	Co : Th	$\triangle\cdot10^3$
4.76	4.72	1.008	—4.2
5.23	5.18	1.009	—3.2
10.01	9.85	1.015	+2.8
21.02	20.70	1.014	+1.8
29.78	29.31	1.015	+2.8
	$\bar{x}$ =	1.0122	

$$S^2 = 11.7\cdot10^{-3}$$

100 ml volume
10 ml acetic acid 2*M*
10 ml Na-acetate 1*M*
1.5 ml al.-S ind. 0.1%

References p. 240.

Standardisation of the Complexone and thorium nitrate solution

The Complexone solution is standardised with pure zinc. To this end about 1 g is weighed exactly and dissolved in a little HNO_3 1 : 2. After boiling and cooling follows dilution to 100 ml.

10 ml are pipetted into an Erlenmeyer flask of 500 ml capacity and diluted to about 250 ml. When the solution has only a low acidity, 12½ ml buffer solution (350 ml ammonia 25% + 54 g NH_4Cl diluted to 1 l, pH about 10) are added at once; otherwise the solution is nearly neutralized with NaOH until just no precipitation is formed and then buffer solution is added.

Then follows titration with Complexone solution adding at the same time a small quantity of eriochrome black T (2-3 mg) as indicator. The end point is reached when the solution is a pure blue. The colour change in the titration is very sharp.

The titre of Complexone determined in this way is within a few tenths per cent in accordance with the one found by the titration of a known quantity of Ni, Ca or Mg[2]. Only once had we a c.p. preparation of Complexone with which greater differences in titre (more than 1%) occurred; a purification of the Complexone by precipitating the free acid once and afterwards dissolving again in a little NaOH was sufficient to eliminate the differences in titre.

Now the titre of thorium nitrate can be determined by means of the Complexone solution in the way described under Procedure. To increase the accuracy the forward and backward titration can be applied with advantage (see page 238).

The determination of thorium

Perhaps it is possible to use the titration method for thorium determination. In our experiments (only by way of orientation) we determined the ThO_2 in pure thorium nitrate, both according to the loss on ignition at 1000°C [5] method and according to the titration method. We abandoned judging the correctness of the results of both methods*.

For the determination of thorium in impure material a separation beforehand will be necessary as a rule, as other metal ions also react at pH 2.8-3.5.

The values found are specified in Table II.

In further articles we shall describe the application of this reaction to the determination of Al, Ni and Bi.

We express our thanks to the Management of the N.V. Philips' Gloeilampenfabrieken for their consent to this publication.

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* During the preparation of this publication a report on a lecture about the titration of Th with Complexone was edited.
J. S. FRITZ AND J. J. FORD, Pittsburg Conf. March 1953. *Anal. Chem.*, 25 (1953) 521.

TABLE II

COMPARATIVE DETERMINATIONS OF ThO_2 IN THORIUM NITRATE ACCORDING TO LOSS ON IGNITION AND THE TITRATION METHOD

Sample	% ThO_2 loss on ignition	% ThO_2 titration	△. in % relative
A	47.0	46.6	—0.8
A	47.0	46.6	—0.8
B	49.5	48.5	—2
C	48.0	47.7	—0.6
D	46.3	46.2	—0.2

SUMMARY

The reaction between thorium and Complexone III (disodium salt of ethylenediaminetetra-acetic acid) at pH 2.8-4.3 has been developed to a quantitative method. As indicator alizarin-S is used. In the first place the reaction is suitable to back-titrate an excess of Complexone III in the pH range mentioned and it is the basis for an Al, Ni and Bi determination still to be published; moreover, it probably presents the possibility of a simple determination of thorium.

RÉSUMÉ

La réaction thorium-complexon III (sel disodique de l'acide éthylènediaminotétracétique), aux pH 2.8 à 4.3, est proposée pour le dosage du thorium. On utilise comme indicateur l'alizarine S. Cette méthode convient pour un dosage indirect (titration du complexon III en excès aux pH indiqués) et pour le dosage de Al, Ni et Bi (à paraître ultérieurement). Il y a également possibilité d'un dosage direct du thorium.

ZUSAMMENFASSUNG

Die Reaktion zwischen Thorium und Complexon III (dem Dinatriumsalz der Äthylendiamintetraessigsäure) bei pH 2.8-4.3 wurde zu einer quantitativen Methode entwickelt. Als Indikator wurde Alizarin-S benützt. Die Reaktion ist in erster Linie geeignet um einen überschuss von Complexon III in dem erwähnten pH-Bereich zurückzutitrieren und gibt eine Grundlage für eine noch zu veröffentlichende Al-, Ni- und Bi-Bestimmung; darüber hinaus bietet sie wahrscheinlich die Möglichkeit zu einer einfachen Thoriumbestimmung.

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ÜBER DIE ABHÄNGIGKEIT DES VERLAUFS DER PERCUPRIMETRISCHEN TITRATIONSKURVE VON DER KONSTITUTION DER PROTEINE

von

G. BECK

Medizinisch-chemisches Institut der Universität, Bern (Schweiz)

In einer Reihe von Arbeiten ist gezeigt worden[1], dass das Kaliumcupri-3-perjodat $K_7[Cu(JO_6)_2]$ und das Kaliumcupri-3-tellurat, Verbindungen, die das Kupfer in dreiwertiger Form enthalten, im Stande sind Proteine in alkalischer Lösung oxydativ abzubauen. Bei dieser Reaktion werden die verschiedenen Peptidbindungen in ganz bestimmter Reihenfolge angegriffen und mit sehr verschiedenen Geschwindigkeiten oxydiert. Zuerst werden die stark reduzierenden Cysteingruppen oxydiert, dann folgen als nächste die Glutaminylbindungen mit stark verlangsamter Geschwindigkeit und anschliessend in rascherer Reaktion die übrigen Peptidbindungen wie namentlich Glycyl-, Alanyl- und Leucylgruppen. Wenn man daher die percuprimetrische Titration eines Proteins in eine Reihe von sukzessiven Teiltitrationen auflöst und deren Geschwindigkeit mit dem Photometer misst, so erhält man für jedes Protein eine charakteristische glockenförmige Zeitreaktionskurve.

Wir haben nun eine Reihe von Serumproteinen bei verschiedenen Krankheiten untersucht, und dabei gewisse Abweichungen von dem Kurvenverlauf von normalen Serumproteinen festgestellt. Um diese Abweichungen besser deuten zu können, wurden verschiedenen Proteine von unterschiedlicher Zusammensetzung und Konstitution untersucht.

Dazu wurden je 20 mg in ca 20 ml Wasser suspendiert und mit 5 ml 40%iger Kalilauge gelöst in einem zylindrischen Glasgefäss, wie man sie für die Blutzuckerbestimmung nach HAGEDORN-JENSEN benutzt und im Photometer nach HILGER UND WATTS oder LANGE untersucht. Vorgeschaltet wurden die Filter violett 601 vom Spekker von Hilger London. Da der Photostrom ausserordentlich schwach war, wurde an den Lange'schen Apparat ein Multiflex-Galvanometer angeschlossen und mit der grossen Blende das Galvanometer auf 100 geschaltet, die linke leere Kammer geschlossen und das Gefäss mit der alkalischen Lösung in die rechte Kammer gestellt. Dies wurde oben durch eine Kartonscheibe fixiert. Da das Galvanometer auf die empfindlichste Stufe geschaltet werden musste, so wurden die Messungen im Dunkelraum bei konstanter Beleuchtung ausgeführt, denn die rechte Kammer durfte wegen dem Rühren und Einspritzen der Lösung nicht geschlossen werden. Zur bessern Konstanthaltung der Temperatur wurde das Glasgefäss mit den alkalischen Proteinlösungen in ein rechteckiges Gefäss aus Plexiglas gestellt, das gerade in die Kammer passte und mit Wasser von 20° gefüllt war.

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[1] G. BECK, *Mikrochemie*, 35 (1950) 169; 38 (1951) 1; 39 (1952) 23; 40 (1953) 258.

Durch Einspritzen von 0.2 ml der dunkelbraunen *N*/150 Kaliumcupri-3-telluratlösung in die alkalische Proteinlösung kann das komplementäre violette Licht nicht mehr auf die rechte Photozelle gelangen, infolge dessen der Galvanometerzeiger auf ca. 170 ausschlägt. Im gleichen Moment wird auch die Stoppuhr in Gang gesetzt. Infolge der allmählich erfolgenden Reduktion des dreiwertigen zum zweiwertigen Kupfer entstehen mit dem überschüssigen Protein violette Komplexe, das Licht kann in gleichem Masse die Lösung wieder passieren und der Galvanometerzeiger fällt mit entsprechender Geschwindigkeit auf die Ausgangslage von 100 zurück. Im Moment, wo er auf 107, der Skala zu stehen kommt wird die Zeit gestoppt und in einem Koordinatensystem eingetragen. Dann wird wieder 0.2 ml Cu(III) eingespritzt und so fortgefahren, bis infolge einsetzender Trübung das Galvanometer nicht mehr genügend ausschlägt.

DISKUSSION DER KURVEN

Durch die Untersuchung von verschiedenen Proteinen sollte der Einfluss der Zusammensetzung und der Konstitution auf den Verlauf der Titrationskurve geprüft werden. Bei der percuprimetrischen Titration von Globulin und Albumin im Serum von Gesunden wurden die Kurven 1 und 2 erhalten. Es wurde vermutet, dass das glockenförmige Maximum in erster Linie dem Gehalt dieses Proteins an Glutaminylbindungen zu verdanken sei und dass die deutliche Vorstufe zwischen 0, bis 1 bzw. 0 bis 2 ml dem Gehalt an Cysteinylgruppen zuzuschreiben sei, z.T.

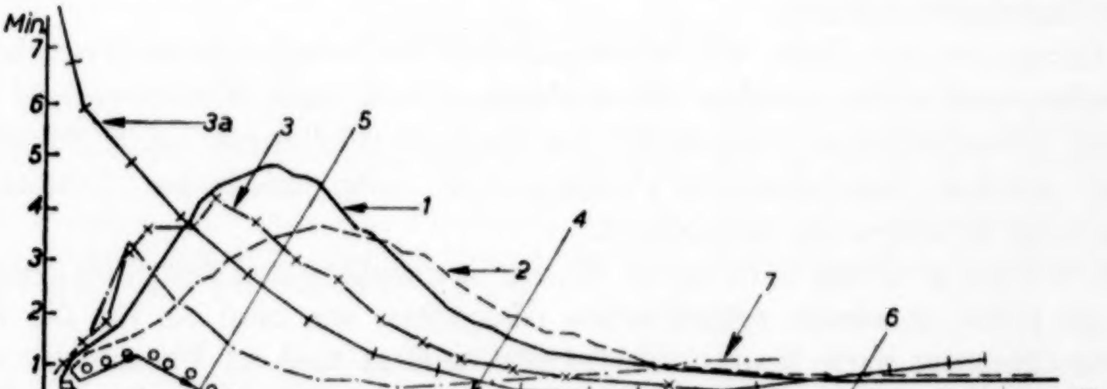

Abb. 1. Titrationskurven von (1) Serumglobulin; (2) Serumalbumin; (3) Erepsin; (3a) Gelatine; (4) Pepsin; (5) Papain; (6) Lipase; (7) Lab

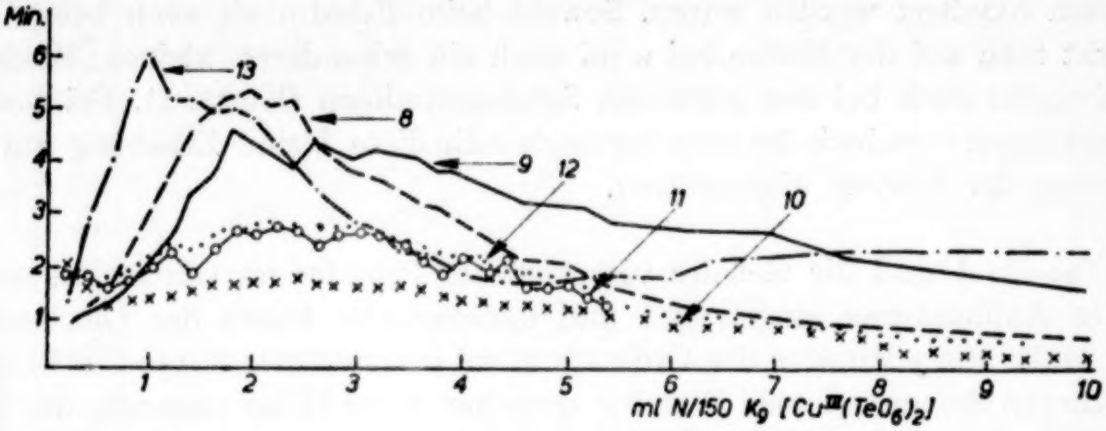

Abb. 2. Titrationskurven von (8) Myosin Kaninchen; (9) Myosin Kalb; (10) Protamin in 50 ml H_2O; (11) Protamin in 10 ml H_2O; (12) Protamin in 30 ml H_2O; (13) Gliadin

eventuell auch dem Tyrosin. Es wurde schon früher darauf hingewiesen, dass beim Gluthation die Cysteinylbindungen zu erst mit dem dreiwertigen Kupfer reagieren. In der Tat haben denn auch die Cysteinfreien Proteine wie Pepton und Gelatine keine solchen Vorstufen auf ihren Kurven, sondern diese fallen direkt von einem Maximum herunter auf niedrige Werte (vgl. Kurve 3a). Des weiteren wurde beobachtet, dass bei Carzinosen die Maximalphasen deutlich verschmälert sind. Die Vermutung, dass diese Maximalphase in erster Linie von den Glutaminylbindungen herrühre, wurde gestützt durch die Tatsache, dass Proteine mit wenig Glutaminsäure viel flacher verlaufen, so beim Spongin, Seidenfibroin, Globin aus Hämaglobin. Umgekehrt weisen Gluten, Casein, Edestin und Vitellin mit hohem Gehalt an Glutaminsäure den höchsten Wert auf. Vom Edestin, das fast die gleiche prozentuale Zusammensetzung aufweist wie das Casein, wurde auch fast dieselbe Kurve erhalten. Das eine Präparat war mehrere Jahrzehnte alt und gab eine Kurve mit viel steilerem Anstieg als das frischere, weil offenbar die stark reduzierenden Gruppen wie z.B. die des Cysteinyls in dem langen

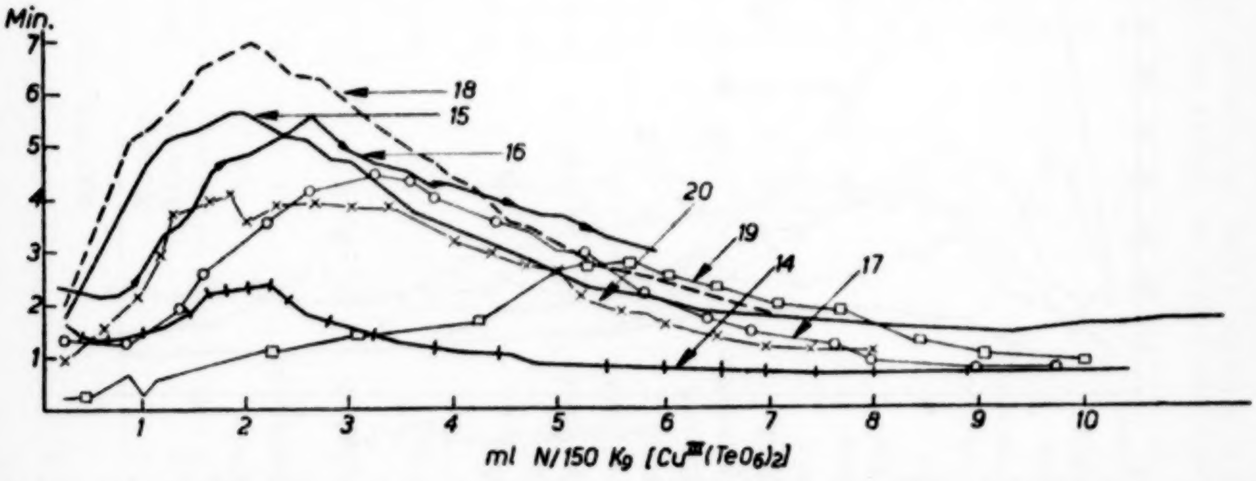

Abb. 3. Titrationskurven von (14) Pseudomucin; (15) Casein; (16) Vitellin; (17) Frauencasein; (18) Paracasein; (19) Ovomucoid; (20) Gliadin

Zeitraum oxydiert worden waren. Sowohl beim Edestin als auch beim Casein bemerkt man auf der Kurve bei 2 ml noch ein sekundäres kleines Maximum, wie übrigens auch bei den normalen Serumglobulinen (Kurve 1). Bei gewissen Erkrankungen verschwindet beim Serumglobulin diese kleine Erhebung auf dem Maximum der Kurven (Cancerosen).

In Tabelle I sind die Gehalte verschiedener Proteine an Glutaminsäure und anderer Aminosäuren eingetragen und daneben die Breite der Glockenkurve in der Höhe von 3 Minuten der Ordinate in ml verbrauchter $N/150$ Cu^{+3}-Lösung. Die Kurven der ersten vier Proteine erreichen diese Höhe nirgends, die Breite ist also null, und bei diesen Proteinen kommt Glutaminsäure nicht vor. Die beiden nächsten Proteine Keratin und Spongin weisen grössere Gehalte an Glutaminsäure auf, ihre Kurven erreichen aber die Höhe von 3 Minuten nicht. Diese Proteine lösen sich aber nicht ohne weiteres in verdünnter Kalilauge. Dies geschieht erst beim Erwärmen unter tiefer greifender Veränderung ihrer Konstitution, so dass diese beiden Beispiele nicht zum Vergleich herangezogen werden können. Die in der Tabelle nun folgenden Eiweisse weisen in der Höhe von drei Minuten eine gewisse Breite der Kurve auf, und diese enthalten auch grössere Mengen Glutaminsäure. Beim Seidenfibroin mit 2% Glutaminsäure reicht die Kurve mit 0.2 ml Breite gerade über die Dreiminutengrenze, sie senkt sich dann rasch und bleibt in geringer Höhe lange konstant gleichmässig. Das Seidenfibroin besteht zu etwa 80% aus dem Tetrapeptid Glycyl-alanyl-glycyl-Tyrosin. Die Glycyl-alanyl-Peptidbindungen werden sehr rasch von Cu^{+3} angegriffen und dem entspricht der tiefliegende und gleichmässige Verlauf der Kurve. Beim Gluten mit 36% Glutaminsäure kann die Kurve bis auf elf Minuten Höhe steigen, wenn man das Protein möglichst schonend in Lösung bringt. Auch die Arginylbindungen reagieren schnell, wie man am Beispiel des Protamins

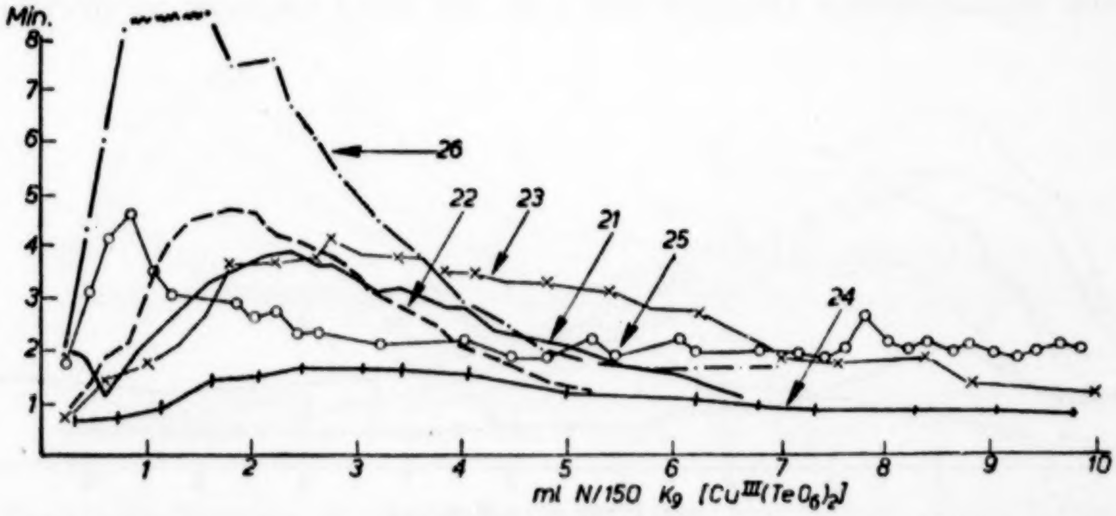

Abb. 4. Titrationskurven von (21) Gluten + Protamin 20 mg; (22) Gluten bei 50° in KOH gelöst + 5 mg Protamin; (23) Laktalbumin; (24) Keratin; (25) Hefenuklein; (26) Gluten

TABELLE I

BREITE DER GLOCKENKURVE IN ABHÄNGIGKEIT VOM GLUTAMINYLGEHALT

Protein	Maxim. Minut.	Brt.	Glt.	Glk.	Aln.	Leuc.	Arg.	Lys.	Tyr.	Ser.	Asp.	Prol.	Cyst.
Protamin	2.6;2.7	0	0				87		10	10		10	
Pseudomucin	2.3	0	0.6	1		4		3					30 Glksa.
Ovomucoid	2.8	0				4						2	26 Glksa.
Elastin	2.5	0	1	26	7	21	4		1			2	7 Phena.
Keratin	1.5	0	8	6	4	15	4	2	4	1	3	4	10
Spongin	2.5	0	18	14	1	8	6	4				6	
Hefenuklein	4.6	1.4	20										
Seidenfibroin	3.2	0.2	2	46	30	2	1	1	12	16	3	1	
Globulin	5	2.5	10	4	2	18	5	8	7	11		8	3
Paraglobin	4.4	4	9	6	7	20	4	9	3	6	10	4	1
Laktalbumin	4.1	4	13	0	3	20	5	9					2
Albumin	3.7	3.6	17	0	3	12	5	12	5	4	10	5	5
Myosin	4.4	3	22	2	7	16	7	12			9		4
Edestin	4.8; 5.4	5;3.6	21	4	4	20	17	2	4	6	12	4	1
Vitellin	5.7	5	22	2	3	16	8	5	5		1	1	2
Casein	5.6	4	22	3	3	15	4	8	6	6	7	11	0.3
Paracasein	7.0	5											
Frauencasein	4.3	3.5					4	7					
Gluten	11; 6	4	36	2	6	6	0	2	4	1	2	0	1
Gliadin	6	3	46	1	3	11	4	0	3	6		14	3
Gelatine	9	2.2	10	24	9	7	9	5	0	3	6	28	0

Es bedeuten: Brt. = Breite der Glockenkurve in 3 Minuten Höhe in ml; Glt. = Glutaminsäure; Glk. = Glykokoll; Aln. = Alanin; Leuc. = Leucin; Arg. = Arginin; Lys. = Lysin Ser. = Serin Asp. = Asparaginsäure; Prol. = Prolin; Cyst. = Cystein + Cystin; Glksa. = Glykosamin; Phena. = Phenylalanin.

sieht, das zu 87% aus dieser Aminosäure besteht, und dessen Kurve die Höhe von 3 Minuten nie erreicht.

Andrerseits ist aber die Breite der Kurve bei der Höhe von drei Minuten nicht streng proportional dem Glutaminylgehalt. Es kann die Glutaminsäure mit verschiedenen Aminosäuren verknüpft sein, und dieser Umstand wird die Kurve in verschiedener Richtung hin beeinflussen. Es wurden auch ein Jodcasein und ein Jodalbumin mit 7 und 11% Jod untersucht. Die betreffenden Kurven weisen einen viel steileren Anstieg auf, da beim Jodieren die Cysteinylgruppen oxydiert wurden. Pepsin und Lab haben nur eine kleine Glockenkurve, bei der Lipase ist sie etwas grösser. Auch die zugehörigen Biuretzahlen sind relativ klein, wie in Tabelle II angegeben ist. Es handelte sich um technische Produkte, die viel Ballaststoffe enthalten. Beim Ovomucoid und beim Pseudomucin tritt das Maximum relativ spät auf. Diese Proteine enthalten 25—30% Glukosamin, und dieses wird offenbar zuerst und zwar in schneller Reaktion oxydiert. Wenn man Gluten mit Protamin (je 20 mg) gemischt titriert, so erhält man stark erniedrigte Kurven (Nr 21 und 22), weil die Arginylbindungen offenbar vor den Glutaminylbindungen oxydiert werden.

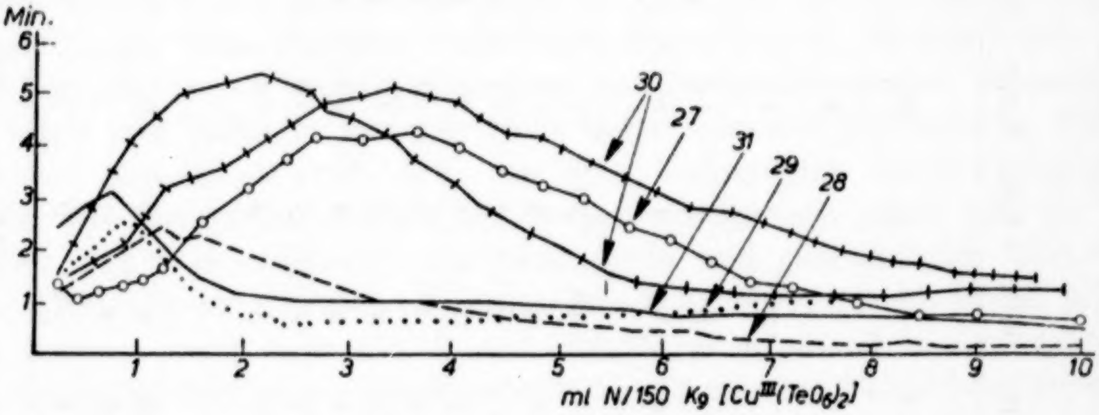

Abb. 5. Titrationskurven von (27) Paraglobin; (28) Elastin I + II; (29) Spongin; (30) Edestin; (31) Seidenfibroin

TABELLE II

BIURET- UND TRÜBUNGSPUNKTE VERSCHIEDENER PROTEINE (20 mg)

Protein	BP	TP	Protein	BP	TP	Protein	BP	TP
Protamin	24.0	24.0	Albumin	16.2	33.5	Gluten	12.0	33.6
Pseudomucin	10.8	12.0	Myosin a	27.5	54.0	Gliadin	15.2	24.0
Ovomucoid	17.4	16.8	Myosin b	35.0	60.0	Erepsin	22.8	36.0
Elastin	18.0	40.8	Vitellin	20.8	30.0	Papain	18.0	42.0
Seidenfibroin	37.0	75.0	Casein	19.8	27.6	Lipase	15.0	38.4
Globulin	16.8	42.0	Paracasein	18.6	43.2	Pepsin	13.8	42.0
Paraglobin	18.0	38.0	Frauencas.	18.0	18.0	Lab	6.0	9.0
Laktalbumin	24.0	36.0	Edestin	26.6	21.0	Gelatine	21.5	45.0

BIURET- UND TRÜBUNGSPUNKTE

Wie schon früher erwähnt werden die Proteine von den Komplexen des dreiwertigen Kupfers oxydativ abgebaut, wobei das zur zweiwertigen Stufe reduzierte Kupfer mit dem überschüssigen Protein violette Biuretkomplexe liefert. Indem Masse, wie das Protein abgebaut wird, geht die violette Farbe zurück und es entstehen blau gefärbte Komplexe. Bei weiterer Oxydation werden auch diese Verbindungen zerstört, das Kupfer wird nicht mehr komplex in Lösung gehalten, und es beginnt sich von einem bestimmten Punkte an eine feine Trübung zu bilden, die sich auf weiteren Zusatz von Kaliumcupri-3-perjodat immer mehr verstärkt und schliesslich wird das dreiwertige Kupfer nicht mehr reduziert. Wir nennen den Punkt des Titrationsverlaufes bei dem sich die erste Trübung einstellt und auf weiteren Zusatz des Reagenses sich weiter verstärkt, den Trübungspunkt. Sehr oft treten schon am Anfang der Titration feine Vortrübungen auf, die sich aber zum Unterschied der eigentlichen Trübung im weiteren Verlauf der Titration nicht verstärken und die man am besten abzentrifugiert. Den Übergang von violett nach blau kann man am besten beim Betrachten gegen eine blaue Tageslichtlampe bestimmen, ebenso den Trübungspunkt, den man am Auftreten eines Tyndalkegels erkennen kann. Die Vortrübungen entstehen wahrscheinlich durch Abscheidung eines sehr schwerlöslichen Kupfersalzes, das nicht komplex in Lösung gehalten werden kann. Beim Hefenuklein konnte der Biuretpunkt, d.h. der Übergang von violett nach blau nicht bestimmt werden, da sich die Lösung von Anfang an stark trübte. Wie man aus Tabelle II ersehen kann, ist der Biuretpunkt von Pseudomucin relativ klein, da dieses Protein mehr als 30% Glukosamin enthält, und die niedrigen Werte von Lab, Pepsin und Lipase rühren davon her, dass diese technischen Stoffe stark verunreinigt sind. Den höchsten Wert weist das Seidenfibroin auf. Dieses Protein besteht zu 80% aus dem Tetrapeptid Glycyl-alanyl-glycyl-tyrosin. Glycin und Alanin sind die zwei Aminosäuren mit dem kleinsten Molekulargewicht, und das Seidenfibroin enthält daher pro Gewichtseinheit am meisten Peptidbindungen, verbraucht daher am meisten Titrierlösung bis zum Erreichen des Biuretpunktes. Die Gruppe Casein, Vitellin und Paracasein besitzt ungefähr die gleiche Zusammensetzung und besitzt auch die nahe beieinander liegenden Biuretpunkte 19.8 20.8 und 18.6. Beim Edestin tritt der Trübungspunkt bereits vor dem Erreichen des Biuretpunktes auf. Das Myosin aus dem Muskeleiweiss hat deutlich zwei verschiedene Werte, je nachdem es aus dem entspannten (a) oder aus dem kontrahierten Muskel (b) stammt. Arginin erhöht den Biuretpunkt deutlich, wie beim Protamin und Edestin und dem Vitellin im Vergleich zum Casein ersichtlich ist, die Glutaminsäure setzt in erwartungsgemäss herab, z.B. bei Gluten und Gliadin.

ZUSAMMENFASSUNG

Durch differentierte Titration der Proteine mit Kaliumcupri-3-tellurat oder Kaliumcupri-3-perjodat erhält man charakteristische Zeitreaktionskurven, aus denen man gewisse Schlüsse auf die Konstitution ziehen kann. Die Reaktionszeit kann im Photometer genau bestimmt werden. Die Bestimmung der Biuretpunkte gibt einen Anhaltspunkt über die Zahl der Peptidbindungen auf eine bestimmte Gewichtseinheit.

SUMMARY

By means of differential titration of proteins with potassium tellurocuprate(III) or potassium periodatocuprate(III) characteristic curves are obtained, from which it is possible to deduce the constitution of the proteins. The duration of the reaction can be determined accurately with a photometer. The determination of the biuret point gives an idea of the number of peptidic bonds per unit of weight.

RÉSUMÉ

Par titration différentielle des protéines au moyen de tellurocuprate(III) de potassium ou de periodatocuprate(III) de potassium, on obtient des courbes caractéristiques, grâce auxquelles on peut tirer des conclusions au sujet de leur constitution. La durée de réaction peut être déterminée exactement au photomètre. La détermination du ,,point de biuret'' donne une idée sur le nombre de liaisons peptidiques par unité de poids.

Eingegangen den 8. Mai 1953

THE ORIGIN OF SOME METHODS OF QUANTITATIVE ORGANIC ANALYSIS VIA FUNCTIONAL GROUPS

by

MORITZ KOHN*
New York (U.S.A.)

(Translated by HENRY M. LEICESTER, *College of Physicians and Surgeons, San Francisco (U.S.A.))*

Elementary analysis, that is the determination of the elements contained in an organic compound, and the determination of the molecular weight give the empirical formula of this compound. Sometimes, however, these results are not enough, since different empirical formulas may be possible. The question of the composition of the substance can, in some cases, only be decided by the determination of certain atomic groups. Such determination of these different atomic groups leads us already into the field of a determination of constitution. Sometimes it is enough to determine only one atom group, in order to indicate analytically the occurrence of a definite chemical compound. Hence, in the course of time, the determination of different functional groups has become an indispensable part of organic analysis. In what follows will be described the development of the determination of methoxyl (alkoxyl) groups, methyl imide (alkyl imide) groups, and the introduction of a method for determining double bonds in unsaturated compounds (iodine number, double bond number).

SIMON ZEISEL (1854-1933) was occupied in the second chemical laboratory of the University of Vienna with a study of the alkaloid colchicine[10] from the seeds of the autumn crocus. By elementary analysis he had established the composition $C_{22}H_{25}O_6N$. He had also shown that when heated with dilute acids, colchicine yielded colchiceine and methanol:

$$C_{22}H_{25}O_6N + HOH = C_{21}H_{23}O_6N + CH_3OH$$

ZEISEL had next converted the methanol formed in this reaction into methyl iodide by the action of hydrogen iodide, and he attempted to weigh the methyl iodide; but because of the great volatility of the iodide, he obtained no usable results. Then it occurred to him to conduct the vapor of the methyl iodide into an alcoholic silver nitrate solution and to weigh the silver iodide which formed.

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* Present address: 536 W. 113 Str. New York 25, N.Y. Paper presented in the Division of Analytical Chemistry at the meeting sponsored by the American Chemical Society in New York on Feb. 8, 1952.

Thus was produced his methoxyl determination, which later became famous. This work *"On a Method for the Quantitative Determination of Methoxyl,"* was presented at the December 17, 1885, meeting of the Vienna Imperial Academy of Sciences[11] by Prof. Ad. Lieben (1836-1914) whose assistant Zeisel then was. Zeisel indicated that in the plant kingdom there were a great number of organic compounds which contained a methyl ether group and that as phytochemistry (the chemistry of plants) advanced, the number of naturally occurring methyl ethers would be expected to increase. He continued: "In many cases the study of such natural products has been very difficult. It often required very circuitous methods to recognize that, apart from the functions of the other atoms in the molecule, some oxygen and carbon atoms occurred as methoxyls, and how many methoxyl groups were present. A positive and convenient method for determination of methoxyl, which at the same time is independent of the occasional physical difficulties and the often very great activity of the dimethylated compounds, seems to me to be of some use for the study of such plant substances and their derivatives as well as for the study of analogous synthetic compounds."

This prediction has been completely fulfilled. To test the usefulness of his methoxyl determination, Zeisel next used substances whose methoxyl content was already known. Zeisel's colleague, Guido Goldschmiedt[3], was then carrying on in the first chemical laboratory of the University of Vienna his basic studies which completely explained the structure of papaverine. Goldschmiedt was able to carry out methoxyl determinations on the Zeisel apparatus and thus to establish the papaverine formula which he had already proposed, $C_{16}H_9(OCH_3)_4N$, by determining the methoxyls.

In the Zeisel apparatus, the substance was heated in a boiling flask with hydrogen iodide and the methyl iodide which formed was carried by a stream of carbon dioxide through a long cooler to a Geissler bulb which was filled with

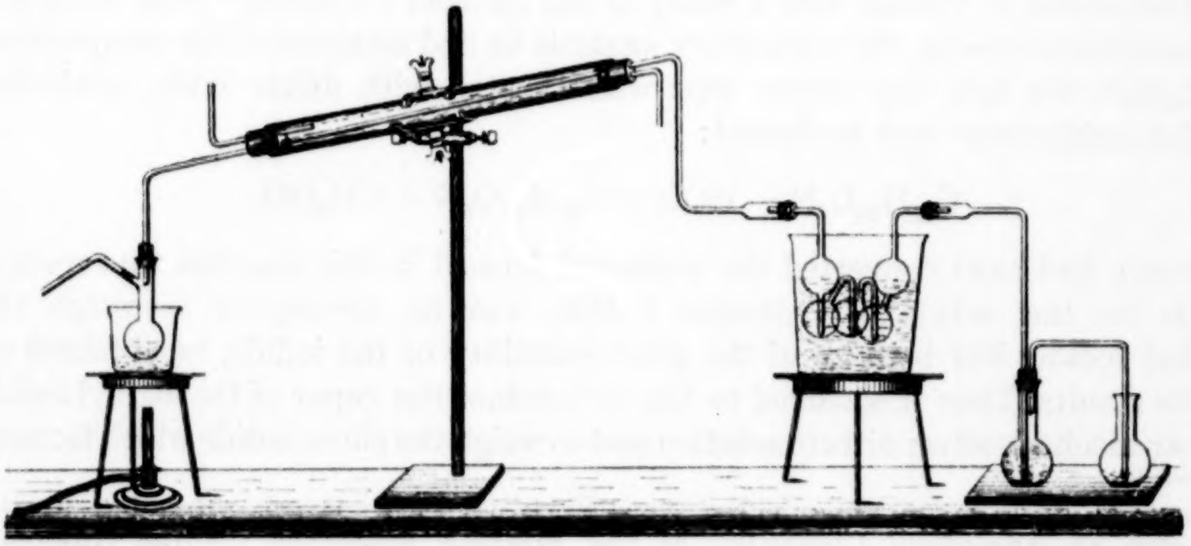

Fig. 1 Zeisel apparatus.

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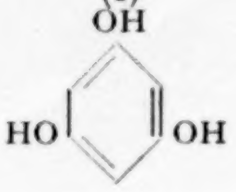
water and red phosphorus, heated by a beaker of warm water. The red phosphorus removed any iodine carried over and the purified methoxyl vapors, led into alcoholic silver nitrate solution, gave silver iodide which was weighed. By this method Zeisel was able to determine that colchicine had the formula $C_{18}H_{13}O_2N$-$(OCH_3)_4$, and colchiceine the formula $C_{18}H_{13}O_2(OH)N(OCH_3)_3$.

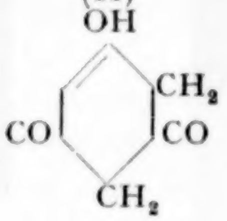
Soon afterwards, Zeisel and Josef Herzig (1853-1924) were able to find use for the ethoxyl determination in their study of bond exchange in phenols[5]. According to the work of Herzig and Zeisel, phenols with meta-hydroxy groups on treatment with potassium hydroxide and ethyl iodide give not only normal ethyl ethers, but also the so-called pseudoethers, in which the ethyl group goes directly onto the carbon.

Thus phloroglucinol (I) with potassium hydroxide and ethyl iodide apparently first forms the tautomers (II) and (III) and then gives pentaethylphloroglucinol (IV) and pentaethylphloroglucinol ethyl ether[5] (V) as well as hexaethylphloroglucinol[5] (VI).

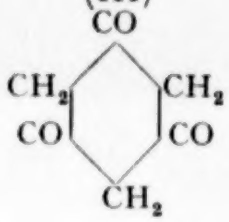
(I)



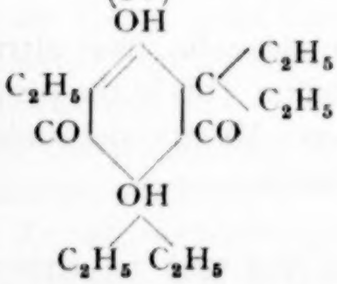
(II)



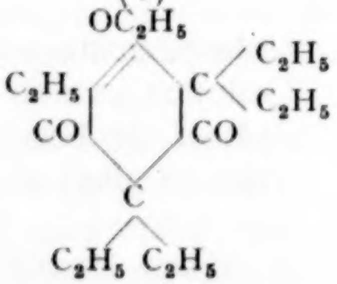
(III)



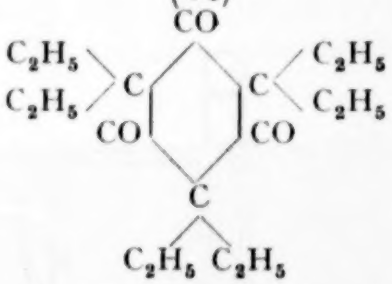
(IV)



(V)



(VI)

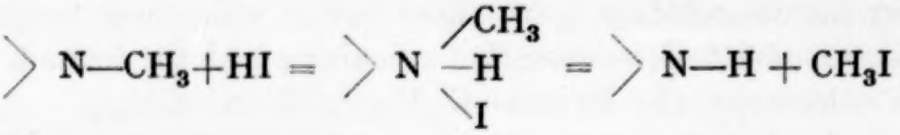


Pentaethylphloroglucinol (IV) and hexaethylphloroglucinol (VI) give no silver iodide in the Zeisel apparatus because they contain no ethoxyl, while pentaethylphloroglucinol ethyl ether (V) gives only one ethoxyl in the Zeisel apparatus.

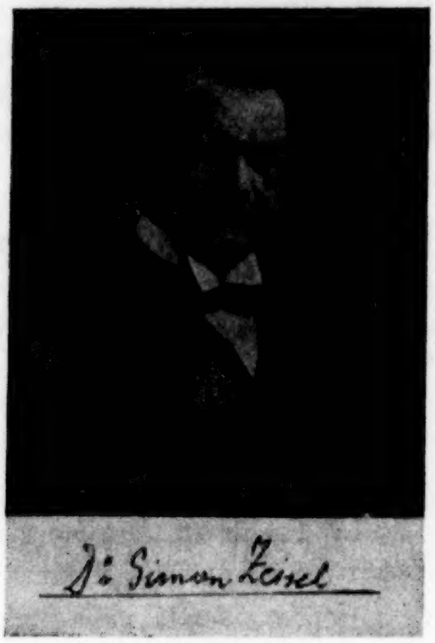
Zeisel was later called to the Hochschule für Bodenkultur in Vienna where he was professor of general and agricultural chemistry from 1892 to 1925. Joseph Herzig, almost contemporary with Zeisel, was assistant to Ludwig von Barth (1839-1890) in the first chemical laboratory of the University. Later Herzig was professor of organic and pharmaceutical chemistry in the University of Vienna from 1897 to 1923.

Zeisel' sassistant in the Hochschule für Bodenkultur, M. J. Stritar[8], described in 1903 a practical apparatus which made the methoxyl determination very easy.

Herzig and Hans Meyer[4] drew an important conclusion from the Zeisel methoxyl determination (1894-1897). They had observed that on heating the hydroiodides of organic bases with ammonium iodide and hydrogen iodide, the methyl or ethyl groups on the nitrogen split off as methyl or ethyl iodide



$$>N{-}CH_3+HI = >N\begin{matrix}CH_3\\ H\\ I\end{matrix} = >N{-}H + CH_3I$$



Dr. Simon Zeisel

JOSEF HERZIG

which, conducted into alcoholic silver nitrate solution, gave silver iodide. This is the principle of the HERZIG AND MEYER determination of alkyl on nitrogen.

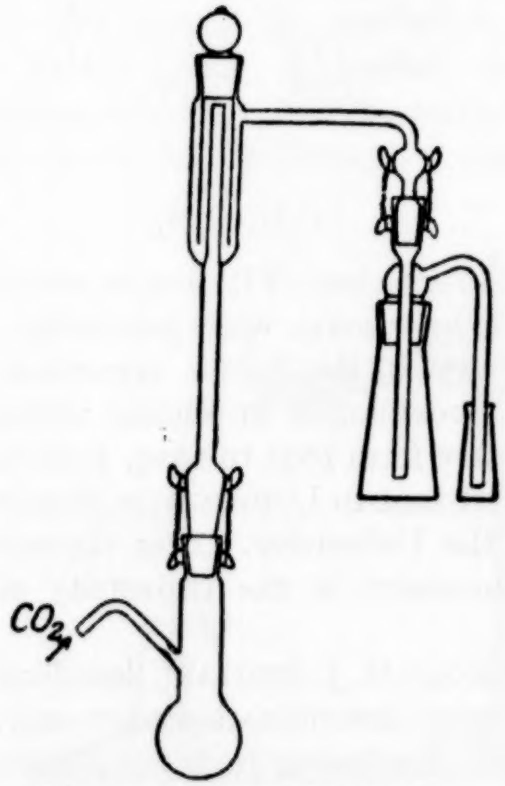


Fig. 2. STRITAR apparatus.

HANS MEYER was assistant to RUDOLF BENEDIKT* from 1894 to 1897 in the chair of analytical chemistry in the Vienna Technische Hochschule. H. MEYER published a book in 1897 on the quantitative determination of organic groups (second ed. 1904, third ed. with E. B. TINGLE 1908, translated into English under the title ***Determination of radicals in carbon compounds***). In 1908 he became professor in the Deutsche Technische Hochschule in Prague, and in 1911 in the German University in Prague. His

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* BENEDIKT was also the teacher of A. v. HUEBL.

Rudolf Benedikt

famous standard work "*Analysis and Constitution Determination of Organic Compounds*" appeared in the fifth edition in 1931. HANS MEYER was born in Vienna in 1872 and died, according to information from Vienna, in a German concentration camp during the Second World War.

ZEISEL AND FANTO have given another new use for the original ZEISEL methoxyl determination. ERLENMEYER[2] had observed in 1866 that heating glycerol under determined conditions with hydrogen iodide converted it to *iso*propyl iodide. ZEISEL AND FANTO[12] made this the basis for a glycerol determination, since the *iso*propyl iodide thus formed gives silver iodide when introduced into an alcoholic silver nitrate solution (1901-1903).

As SCHULZE[7] has shown, this method surpasses all others in accuracy. In this determination, the fat must be first saponified so that the liberated glycerol can be converted to *iso*propyl iodide. WILLSTAETTER AND MADINAVEITIA[9] in 1912 showed that the saponification of fats as ZEISEL AND FANTO suggested was not necessary, but that the fat could be treated directly with hydrogen iodide, which naturally meant a considerable simplication.

ARTHUR VON HUEBL

All the friends, students and fellow workers of HERZIG celebrated his 70th birthday in 1923, and ZEISEL, expressing their good wishes, said that HERZIG was a true advancer of science, an "Auctor scientiarum". HERZIG, in his thanks, said that he had been the greatest beneficiary of the methoxyl determination of his friend ZEISEL. The Academy of Sciences in Vienna in 1924 awarded ZEISEL the functional group prize, saying that they thanked ZEISEL for the most outstanding work in the field of determination of organic groups which had been done by an Austrian. This well deserved recognition came to ZEISEL relatively late, since even in previous years the Vienna Academy of Sciences had awarded prizes for excellent work by Austrian chemists who had been able to carry on

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their work only with the aid of the ZEISEL methoxyl determination.

To another Austrian, A. VON HUEBL (1853-1932), we owe the method for the determination of double bonds in unsaturated compounds, the iodine number (1884). HUEBL was a professional officer and was given leave for the study of chemistry in the Technische Hochschule in Vienna for the years 1879-1881. He had the good fortune to find an outstanding teacher in Rudolf Benedikt (1852-1896).

Even in 1881 there appeared in the Wiener Monatshefte für Chemie a paper by RUDOLF BENEDIKT and Oberleutenant ARTHUR FREIHERR VON HUEBL[1] on "*Di- and trinitroresorcinols.*" Three years later, in 1884[6], HUEBL published his method of determining the iodine number. It consists in treating the unsaturated compound with mercuric chloride and alcoholic iodine solution, so that iodine monochloride adds. The HUEBL method for determining the iodine number is especially good for fats, oils, waxes, ethereal oils, and resins, but is also useful for scientific purposes. HUEBL's teacher, RUDOLF BENEDIKT, who was torn by a tragic fate from his scientific teaching and research in 1896, was an unusually many-sided man. He was indeed professor of analytical chemistry in the Vienna Technische Hochschule, but other branches of chemical science and technical chemistry owe him much. BENEDIKT occupied himself especially with the analysis of fats, and his book "*Analysis of fats and waxes*" appeared in several editions (and in English translation). It is certain that, by his work in BENEDIKT's laboratory, HUEBL became interested in the analysis of fats and waxes. By his method of determining the iodine number HUEBL earned an honored name in the world of chemistry. He later left the field of pure chemistry and turned to photography and photogrammetry. He died in Vienna, in 1932, a lieutenant general and Director of the Military Geographic Institute.

Through the pains of PREGL (1969-1930) methods for the determination of organic functional groups were transformed into micro-determinations. The stimulation due to PREGL and his school has led other chemists also to work out microanalytic methods for functional group determination. The methods described above have already spread before the introduction of micromethods over the whole earth, as far as chemists themselves have gone. The great progress which microanalysis has brought with it has contributed to the international expansion and more abundant use of these methods. Today the old macromethods for the determination of organic groups have been almost completely replaced by the modern micromethods. It is therefore obvious that the publications and textbooks in which these micromethods are described now serve as the most important literature sources in this field, while the work of the pioneers begins to vanish into the dusk of forgetfulness. The Austrian chemists ZEISEL, HERZIG, HANS MEYER, and HUEBL were true pioneers. The iranalytical methods have enormously advanced the work of organic chemists in science and industry in the past, and they will surely do so in the future also.

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ACKNOWLEDGEMENT

The author wants to express his sincere gratitude to Dr. MARIA ZEISEL who presented him with the picture of her father, the late Professor S. ZEISEL, and to the Austrian Kriegs Archiv (Hofrat Dr. OSKAR REGELE) who procured for him the picture of the late A. VON HUEBL.

SUMMARY

The methods of quantitative organic analysis via functional groups have become indispensable in the course of time. The origin of the classical methods of the determination of methoxyl (alkoxyl) (S. ZEISEL, 1885), methyl imide (alkyl imide) (J. HERZIG AND H. MEYER, 1894-1897) and the origin of the method of determination of the double bond number, (iodine number) (A. VON HUEBL, 1884) is explained.

RÉSUMÉ

Les méthodes d'analyses quantitatives des fonctions organiques sont devenues indispensables. L'auteur rappelle les origines des méthodes classiques des dosages des groupements: méthoxyle (alcoxyle) (S. ZEISEL 1885), méthylimide (alcimide) (J. HERZIG ET H. MEYER, 1894-1897) et la méthode de détermination des doubles liaisons (indice d'iode) (A. VON HUEBL, 1884).

ZUSAMMENFASSUNG

Die Methoden zur quantitativen Bestimmung organischer Atomgruppen sind im Laufe der Zeit unentbehrlich geworden. Der Ursprung der klassischen Methoden zur Bestimmung von Methoxyl (Alkoxyl) (S. ZEISEL, 1885), Methylimid (Alkylimid) (J. HERZIG UND H. MEYER, 1894-1897) und der Ursprung der Methode zur Bestimmung der Doppelbindung (Jodzahl) (A. VON HUEBL, 1884) wird geschildert.

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A STUDY OF THE CHROMATOGRAPHIC DETERMINATION OF AMINO ACIDS IN THE PRESENCE OF LARGE AMOUNTS OF CARBOHYDRATE*

by

J. P. DUSTIN, C. CZAJKOWSKA, S. MOORE** AND E. J. BIGWOOD

Laboratory of Biochemistry, Faculty of Medicine, University of Brussels (Belgium)

INTRODUCTION

In the determination of the amino acid composition of whole foods by ion exchange chromatography, as discussed in the preceding paper[1], information is needed on whether the presence of carbohydrate during hydrolysis causes significant losses of amino acids or interferes in the chromatographic analyses. As a first step in such a study, the following experiments have been carried out with synthetic mixtures of amino acids heated with boiling 6N HCl for 22 h with more than a hundred fold quantity of starch or glucose, corresponding to the extreme case of a food containing less than 2 per cent. amino acids in the presence of 97 per cent. starch (*e.g.*, cassava meal[2]). Tryptophan, cystine, and methionine, are all known to be altered under these conditions. Their determinations present special cases discussed in the preceding communication[1]. The present study is concerned with the remaining fifteen most common amino acids.

PROCEDURE

The hydrolysis was performed under dilute conditions[1,6] with 200 ml of glass distilled 6N HCl per 1-2 g of carbohydrate, as in the experiments in which cassava meal was hydrolyzed with about 100 times its weight of acid. Chromatographic analyses were carried out on (a) the initial untreated synthetic mixtures, (b) the amino acids after boiling for 22 h with 6N HCl alone, and (c) the amino acids after the same treatment in the presence of added carbohydrate.

The synthetic mixtures contained 5 to 50 mg quantities of each amino acid

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** Visiting Professor (Francqui Chair) 1950-51. Member of the Rockefeller Institute for Medical Research, New York.

dissolved in 100 ml of 0.1N HCl. For each control analysis, a 2 or 4 ml aliquot of the solution was added to 200 ml of 6N HCl and boiled under reflux for 22 h with or without added carbohydrate. The hydrolysates were concentrated and made to final volume of 10 ml as previously described[1]. The chromatographic analyses were made on 1 or 2 ml aliquots of the final solutions. The chromatography was performed on columns of Dowex-50 by the method of MOORE AND STEIN[3] as employed in this laboratory by SCHRAM *et al.*[1]. Tyrosine and phenylalanine recoveries were determined on 100 cm columns operated from the beginning with pH 4.25 buffer at 75°.

TABLE I

SUMMARY OF RECOVERY EXPERIMENTS
(MIXTURES BOILED UNDER REFLUX FOR 22 h WITH 6N HCl)

Expt. No.	Chromatogram Nos.	Amino acids added to 200 ml 6N HCl	Carbohydrate added	Aliquot of final 10 ml solution chromatographed ml
A	110	None	Starch 2 g	2
B	87	None	Glucose 2 g	2
I	23, 24, 25	Aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, valine, isoleucine, leucine (Total 24 mg)	Starch 2 g	1
II	82, 82 A, 83	Threonine, serine, glutamic acid, proline, glycine, valine (Total 30 mg)	Glucose 2 g	1
III	(a) 29, 30, 32 (b) 39, 41, 42	Aspartic acid, threonine, serine (Total 5 mg)	None	2
IV	56, 57, 58, 59, 62, 65	Tyrosine (1.2 mg)	Starch 2 g (No. 62) Glucose 1 g (No. 65)	2
V	48, 50, 51, 52, 53	Tyrosine, phenylalanine (Total 3.4 mg)	Starch 2 g	2
VI	60, 63, 64, 66, 67	Histidine, lysine, arginine (Total 2.3 mg)	Glucose 1 g	2

RESULTS

The experimental conditions are summarized in Table I. In Expt. A chromatographic analysis was made of a hydrolysate of starch alone, performed as a control to make certain that the starch did not contain significant traces of amino acids which would influence the results. The samples used in all cases were potato starch which had been washed with dilute HCl until nitrogen free, or as

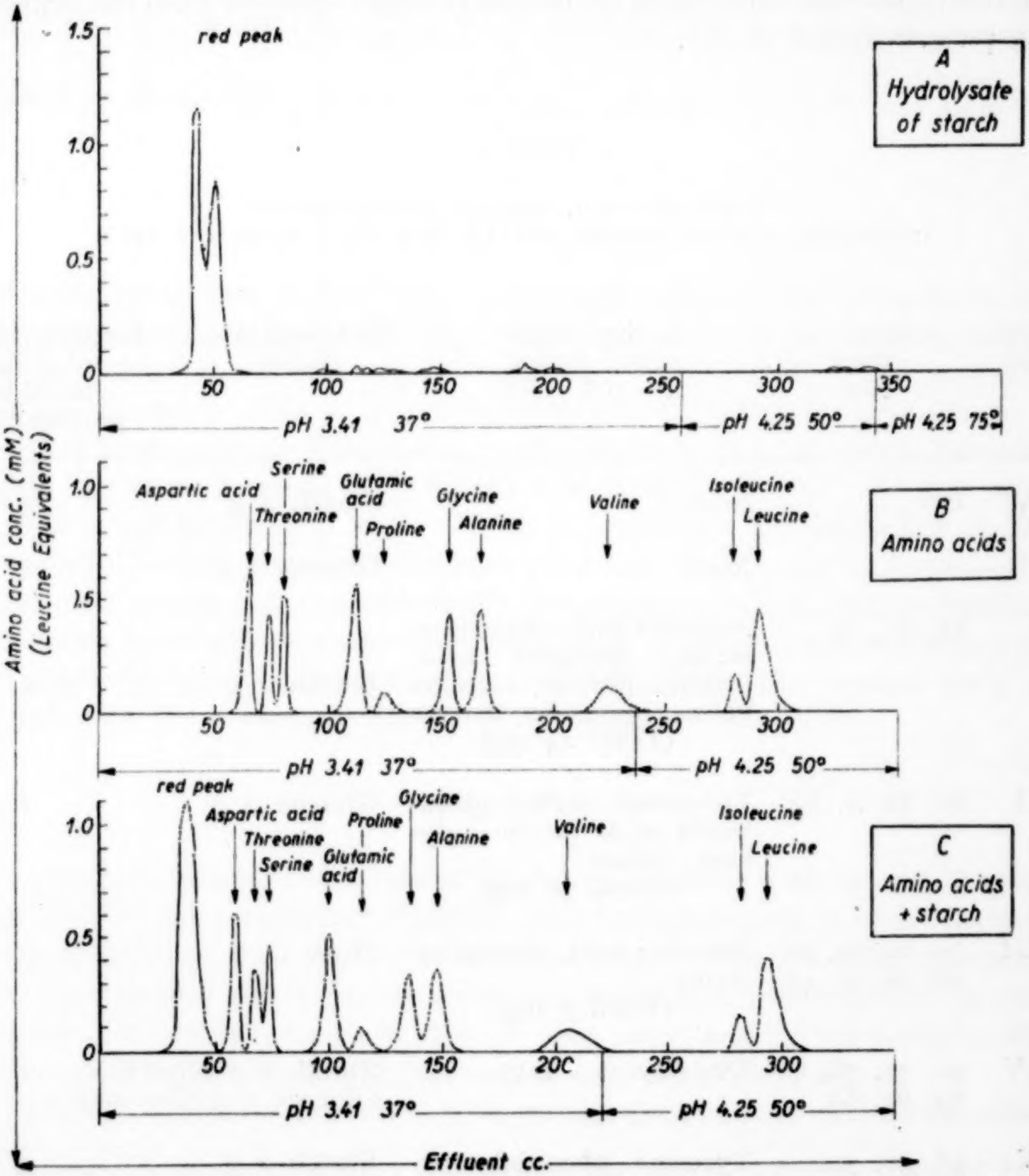

Fig. 1. Comparison of the chromatographic analyses on Dowex-50 of a hydrolysate of starch and a mixture of ten amino acids boiled with 6*N* HCl for 22 h with and without the addition of the carbohydrate (Expts. A and I, Table I). The height of the proline peak in this case, has not been corrected for the color factor.

nearly so as possible. The starch used in Expt. A showed 0.007 per cent. nitrogen by Kjeldahl analysis. The effluent curve obtained with the starch hydrolysate on a 100 cm Dowex-50 column is given in Fig. 1A. The red peak obtained when the effluent fractions are treated with ninhydrin indicates the position of emergence of the major carbohydrate decomposition products[1]. The traces of individual ninhydrin positive components, yielding very small yellowish or blue peaks in the usual amino acid range, amount to less than 3 per cent. of any amino acid to be considered in the subsequent analyses. The curve from the 15 cm Dowex-50 column was negative in the range of the basic amino acids, but showed the starch to contain a small but significant amount of NH_3. Expt. B was the similar control with pure glucose. The curve was almost identical with that in Fig. 1A, with the minute peaks after 100 ml being completely absent. The red peak can appear as a double (Fig. 1A) or a single (Fig. 1C) peak.

The recoveries after the hydrolytic treatment were based in each case upon the amino acid content of the initial synthetic mixture as determined chromatographically. Unless one is certain of the purity of each amino acid used to make up the mixture, the chromatographic analysis is essential as a control. The sample of valine available for this study, for example, was found to contain appreciable amounts of alanine, isoleucine, and leucine. The amino acids used in Expts. III to VI were homogeneous and gave recoveries of 100 ± 3 per cent. of theory on a weight basis.

Representative effluent curves are given in Figs. 1B and 1C, illustrating the chromatograms obtained with a mixture of ten amino acids heated with HCl in the presence and in the absence of starch. The principal carbohydrate decomposition products emerge at a position ahead of the first amino acid peak. The subsequent portions of the effluent curves are qualitatively the same. The quantitative results for the series of experiments are given in Table II. The data lead to the following conclusions:

Effect of carbohydrate. Within the limits of accuracy of the present experiments, the addition of carbohydrate under the dilute conditions of hydrolysis does not cause loss of any of the fifteen amino acids. In not a single instance is the observed recovery relative to that with HCl alone lowered by as much as 3 per cent., even in the presence of the very large excess of carbohydrate. The recoveries in Table II, considered in reference to the objective of the present study, indicate that chromatographic analyses of hydrolysates of whole foods of high carbohydrate content should yield reasonably satisfactory results.

Effect of 6N HCl per se. In order to be able to draw conclusions on possible small losses of a few per cent. of the amino acids as a result of heating with HCl alone it would be necessary to carry out experiments on the extension of the heating times to 48 and 96 h to make the percentage losses more significant. The results in Table II are not sufficiently precise to permit us to draw detailed conclusions on the absolute recoveries, which are of importance when the method is applied to the structural analysis of purified proteins. REES[4] has shown clearly

TABLE II

RECOVERIES OF AMINO ACIDS
HEATED WITH 6N HCl (110°) WITH AND WITHOUT THE ADDITION OF CARBOHYDRATE

		Amino acid analyses (mg per 200 ml 6N HCl)			Average per cent. recovery	
Expt. No.	Amino acid	Control analysis of the mixture	After 22 h in 6N HCl at 110°	After 22 h in 6N HCl + carbohydrate	After 22 h with HCl alone	Treated with HCl + carbohydrate
I	Aspartic ac.	3.46	3.57	3.55	101	103
IIIa		2.20	2.22			
			2.16			
IIIb		2.16	2.18			
		2.20				
I	Threonine	1.64	1.78	1.72	98	105
II		3.20	3.04	3.38		
IIIa		1.32	1.28			
			1.24			
IIIb		1.38	1.30			
		1.42				
I	Serine	1.66	1.73	1.65	98	96
II		2.84	2.60	2.68		
IIIa		1.56	1.58			
			1.54			
IIIb		1.50	1.46			
		1.50				
II	Glumatic ac.	3.68	3.62	3.68	98	100
I	Proline	2.05	1.95	1.94	96	98
II		2.98	2.92	3.02		
I	Glycine	1.44	1.51	1.56	102	104
II		6.30	6.30	6.28		
I	Alanine	2.18	2.18	2.17	100	100
II	Valine	11.24	11.16	11.40	99	101
I	Isoleucine	1.17	1.06	1.09	91	93
I	Leucine	4.52	4.32	4.56	96	101
IV	Tyrosine	1.22	1.18	1.16	100	98
		1.18	1.18	1.14		
V		1.08	1.10	1.04		
			1.08	1.10		
V	Phenylalanine	2.24	2.20	2.26	100	100
			2.24	2.20		
VI	Histidine	0.82	0.74	0.74	93	93
		0.78		0.74		
VI	Lysine	0.77	0.73	0.77	94	101
		0.78		0.79		
VI	Arginine	0.78	0.77	0.77	99	99
				0.78		

that under his conditions for the acid hydrolysis of insulin, serine is decomposed to the extent of 10 per cent. and threonine about 5 per cent. in 24 h, and this finding has been confirmed in chromatographic analyses of insulin hydrolysates by HARFENIST[5]. The average recoveries of each of these amino acids in our experiments with HCl alone is 98 ± 5 per cent. (Table II), but we do not wish to place emphasis on these figures. An accurate study of the recovery of serine and threonine by this method would require extension of the heating time in order to pick up possible cumulative losses of 10 or 20 per cent.

In general, the data in Table II, within the limits of accuracy of the analyses, are in agreement with the knowledge on the stability of most of the amino acids to HCl. The isoleucine figure is low, but rests on a single analysis involving a small peak (Fig. 1). Histidine is the most difficult amino acid to handle quantitatively on Dowex-50 and the low recovery in Expt. VI requires further study.

DISCUSSION

The possible interaction between amino acids and carbohydrates during hydrolysis has been investigated frequently in the past[7] [8].

The determination of the stability of the amino acids themselves in the presence of HCl and carbohydrate is the first step in the study of hydrolytic conditions for food proteins. A further essential step is the study of the recovery of amino acids from proteins of known composition when their hydrolysis takes place in the presence of carbohydrate, to ascertain whether carbohydrate exerts any greater effect on amino acids in protein and peptide combinations than it does on the end products of the hydrolysis under our conditions. The release of amino acids from protein structures introduces a number of still undefined variables (*cf.* MARTIN AND SYNGE[8], BLOCK AND BOLLING[7]). It also remains to be determined whether the unusually dilute conditions of hydrolysis chosen for the present experiments (50 mg of protein per 200 ml of 6*N* HCl) are essential to prevent significant carbohydrate-amino acid interactions, or whether the use of somewhat less acid is also satisfactory. An additional point not considered here is the possible need for longer times of heating for protein hydrolysis. The usual 22 to 24 h is not always sufficient to release the last 10 to 20 per cent. of valine and isoleucine from peptide linkages (CHRISTENSEN[9], SYNGE[10]). HARFENIST[5] recently found that 48 or 96 h hydrolysis of insulin was necessary to obtain complete liberation of valine and isoleucine.

SUMMARY

Synthetic mixtures of 15 of the 18 most common amino acids (cystine, methionine and tryptophan excepted) were boiled with 6*N* HCl in the presence and absence of carbohydrate. The decomposition products from starch and glucose do not interfere with the chromatographic determination of the amino acids on ion exchange columns.

References p. 262.

In no instance was the observed recovery of an amino acid lowered by as much as 3 per cent. by the addition of carbohydrate (2 g) to 25-50 mg of amino acids per 200 ml 6*N* HCl. The dilute conditions of hydrolysis correspond to those adopted for the determination of the amino acid composition of foods of high carbohydrate content.

RÉSUMÉ

Divers mélanges synthétiques de 15 acides aminés parmi les 18 acides aminés usuels (à l'exception de la cystine, de la méthionine et du tryptophane) furent traités à l'acide chlorhydrique 6*N*, bouillant, en présence et en absence d'hydrates de carbone. Les produits de désintégration de l'amidon et du glucose qui en résultèrent n'ont pas interféré le dosage chromatographique des acides aminés sur colonnes d'échangeurs d'ions. Le résultat du dosage s'est toujours montré, lorsque le mélange de 25 à 50 mg d'acides aminés subit le traitement hydrolytique (en présence de 2 g de glucide dans 200 ml de HCl 6*N*) en concordance à moins de 3% près, avec celui obtenu après le même traitement, mais en absence de glucide. Ces conditions de dilution sont celles adoptées pour hydrolyser des aliments riches en glucides en vue du dosage des acides aminés qu'ils contiennent.

ZUSAMMENFASSUNG

Synthetische Mischungen von 15 der 18 üblichsten Aminosäuren (mit Ausnahme von Cystin, Methionin und Tryptophan) wurden mit 6*N* HCl in Gegenwart und Abwesenheit von Kohlenhydraten gekocht. Die Zersetzungsprodukte der Stärke und Glucose stören die chromatographische Bestimmung der Aminosäuren in Ionenaustauschsäulen nicht. In keinem Falle war die beobachtete Ausbeute einer Aminosäure durch den Zusatz von 2 g Kohlenhydrat zu 25-50 mg Aminosäure pro 200 ml 6*N* HCl um mehr als 3% erniedrigt. Die Verdünnungsbedingungen der Hydrolyse entsprechen den zur Bestimmung der Zusammensetzung der Aminosaüren in Lebensmitteln mit hohem Kohlenhydratgehalt übernommenen.

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH CUPROINE

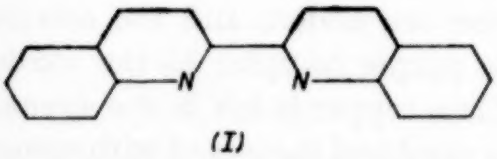
by

J. HOSTE, J. EECKHOUT AND J. GILLIS

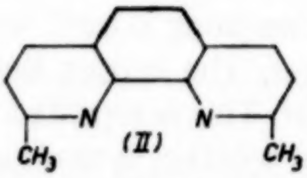
Laboratory of Analytical Chemistry, University of Ghent (Belgium)

INTRODUCTION

HOSTE[1] has demonstrated the conditions that 2,2'-dipyridyl, 2-pyridyl-2'-quinolyl or 2,2'-diquinolyl derivatives must satisfy to form a copper-specific reagent. From the eleven different compounds examined, it appeared that 2,2'-diquinolyl(I), which was called cuproine, is the most favourable reagent for copper for qualitative as well as for spectrophotometric purposes. HOSTE, HEIREMANS AND GILLIS[2] have extended the examination of cuproine and have investigated different factors such as, stability of colour, influence of pH, and influence of the most common anions and cations. From this investigation it appeared at that time that, because of its specificity and great sensitivity, cuproine could be considered as one of the best reagents for copper, especially in the determination of small traces of this element. Since then the copper-specific group has been the subject of many investigations. SMITH AND MCCURDY[3] have studied 2,9-dimethyl-phenanthroline(II), which they called neocuproine. Earlier HOSTE had demonstrated that 6,6'-dimethyl-2,2'-dipyridyl(III) is a specific reagent for



(I)



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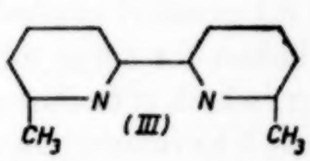

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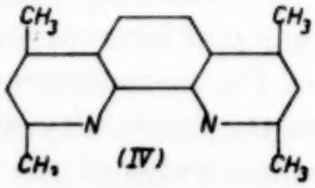

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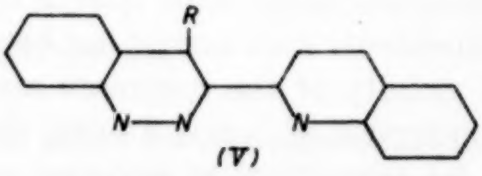

(V)

$R = CH_3OC_6H_4-$

copper, so that it could be expected that 2,9-dimethylphenanthroline would act analogously. The molecular extinction coefficient of this compound is 7950 compared with 6430 for cuproine, which means a greater sensitivity. However, the preparation of this compound, by double Skraup synthesis, is more difficult than that of cuproine. In a later communication[4], the same authors have investigated other polymethylphenanthrolines some of which contain the copper-specific group and are still more sensitive, such as 2,4,7,9-tetramethylphenanthroline(IV), which has a molecular extinction coefficient of 8860.

Irving and Williams[5] have investigated, among others, 3-(2′-quinolyl)-4′-p-methoxycinnoline(V). This compound, which contains the copper-specific group, is also a very sensitive reagent for copper ($\varepsilon = 8500$).

While for some years a copper-specific grouping had remained unknown, one has at one's disposal at the present time a series of new reagents, of which the molecular extinction coefficient of the most sensitive is 8860. Although some of the reagents mentioned are more sensitive than cuproine, it seemed to us that a more penetrating study of this latter reagent is justified, because it is still the easiest, and with good yield, to prepare, *viz.*, by catalytical dehydrogenation of quinoline. The sensitivity is also very high and most satisfactory. Above all the cuproine complex is stable to atmospheric oxidation, which is not the case with some copper complexes of the other reagents.

In this study is given, besides a classical method of determining copper by repeated extraction of the complex with *iso*amyl alcohol, an empirical method, which especially for routine analyses is very useful because it is rapid.

DETERMINATION OF THE EXTINCTION CURVE AND EXTINCTION COEFFICIENT BY (E_{MAX})

Method. 25 ml of an aqueous solution of copper sulphate containing 5.00 μg copper per ml are placed in a shaking flask and treated with some crystals of hydroxylamine chlorhydrate to reduce Cu(II) to Cu(I).

5 ml *iso*amyl alcohol containing 0.02% cuproine are added, and the mixture is shaken for some minutes. The copper forms a purple complex in the alcohol layer, which is decanted off. This is repeated until no copper is left in the aqueous phase. The *iso*amyl alcohol solution is made up to 25 ml and measured with respect to a blank that was prepared in the same way, but without the presence of copper. In this way any impurities in the reagents used are compensated. A Beckman DU spectrophotometer with quartz optics was used as measuring instrument. The measurements were carried out between 400 and 600 mμ at intervals of 10 mμ.

In the vicinity of the minimum and the maximum the measurements were made at intervals of 2 mμ. During the measurements the sensitivity was kept constant (at three turns of maximal sensitivity) while the width of the slit was varied from 0.06 to 0.02 mm. Extinction is maximum at $\lambda = 546$ mμ.

With a slit width of 0.02 mm, corresponding with an effective band width of 1.51 mμ (see Beckman Bulletin 91 F, p. 3), we found, for a layer thickness of 1 cm, $E = 0.506$ (mean of 4 measurements). Hence the molecular extinction coefficient is:

$$\varepsilon = \frac{E}{cd} = 6430$$

(c = molecular concentration; d = thickness of the layer; E = extinction).

The extinction curve obtained is given in Fig. 1.

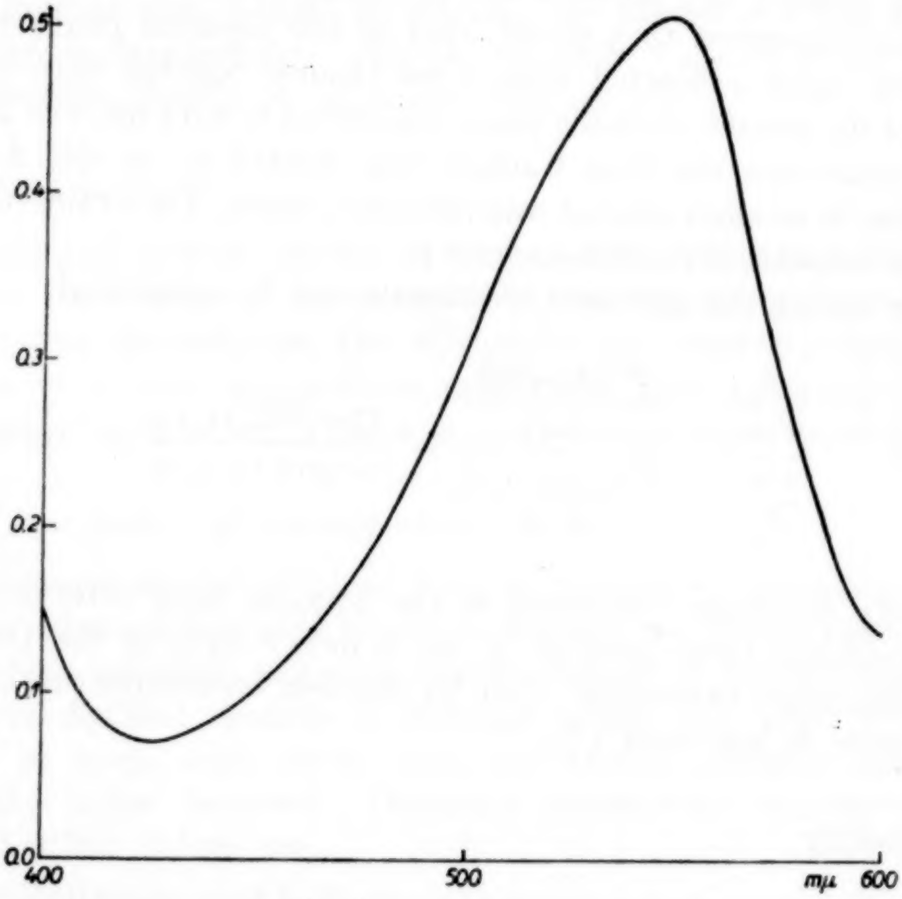

Fig. 1. Extinction curve of the cuproine complex in *iso*amyl alcohol

SYSTEMATIC INVESTIGATION

The influence of different factors that could affect the extinction was examined in detail. All measurements were executed with a Beckman DU spectrophotometer.

References p. 274.

Partition coefficient

The extractibility of the complex with water-insoluble solvents was examined. Amyl alcohol, benzyl alcohol, hexyl alcohol, chloroform, benzene, carbon tetrachloride, *iso*amyl alcohol, ethyl acetate and amyl acetate were some of the solvents used.

*Iso*amyl alcohol gave by far the best partition coefficient, so that this solvent was used in further experiments.

In order to determine the partition coefficient, 50 ml water containing 5 μg Cu per ml were shaken for 3 min at 25° C with 5 ml *iso*amyl alcohol containing 0.08% cuproine. After standing for 30 min, the aqueous layer was removed and centrifuged to remove any small drops of *iso*amyl alcohol. The volume of the alcoholic phase amounted to 3.55 ml, that of the aqueous phase to 51.25 ml. The latter was again extracted with 5 ml *iso*amyl alcohol (0.02% cuproine). The volume of the second alcoholic phase amounted to 5.15 ml. For the measurement of the extinction the first fraction was diluted to 25 ml. A solution of 0.02% cuproine in *iso*amyl alcohol was used as a blank. The extinctions for both fractions were respectively 0.888 and 0.037.

From these values the partition coefficient can be calculated:

$$k = \frac{\dfrac{x}{V_{alc}}}{\dfrac{a-x}{V_a}} = \frac{\dfrac{k' \cdot 25 \cdot 0.888}{3.55}}{\dfrac{k' \cdot 0.037 \cdot 5.15}{51.25}} = \frac{25 \cdot 0.888 \cdot 51.25}{0.037 \cdot 5.15 \cdot 3.55} = 1680$$

The quantity of copper remaining in the aqueous layer after one extraction, with a water/alcohol ratio equal to ± 10, is only 0.85% of the total quantity present. For one single extraction, even for this less favourable ratio of the liquid phases, the error is less than 1%.

Time of shaking

In order to determine the minimum time required for a quantitative extraction, 4 solutions with a copper content of 5 μg per ml were shaken for 40, 50, 60 and 70 seconds. From this it appeared that a shaking time of 50 seconds is sufficient for a volume ratio water/alcohol = 1. For a ratio water/alcohol = 10, the extraction is practically complete after 2 minutes vigorous shaking.

Colour stability

The extinction of the solution obtained was measured over a time interval of 72 h. No appreciable change could be distinguished during this time.

Influence of pH *on the extraction*

From a series of tests adjusted to different pH values by buffer solutions, it appeared that the extraction of the complex is quantitative from pH 2 to 9, so that it is not necessary to bring the solution to be analysed to a definite pH value. A simple control with a universal indicator is sufficient in all cases.

Influence of foreign ions

The following anions and cations, in ratio 1000 to 1 Cu, do not interfere with the determination: Al, As, Ba, Ca, Cd, Co, Fe(III), Fe(II), Li, Mg, Mo(VI), Mn(II), NH_4, Ni, Sb(III), Sn(II), Sr, Ti(IV), V(V), W(VI), Zn, acetate, borate, bromide, chloride, chlorate, perchlorate, tartrate, nitrate, sulphate, and phosphate. The cations were present as nitrates, the anions as alkali salts. Cyanide, rhodanide and oxalate interfere with the reaction. Because of the definite specificity, a previous separation is mostly unnecessary.

Influence of temperature

The solubility of *iso*amyl alcohol in water varies with temperature. Therefore concentration differences of the complex in the organic solvent can originate from temperature fluctuations. The differences are, however, small for a water/alcohol ratio = 1, with temperature differences from 17 to 23°. With a ratio water/alcohol = 10, however, a more accurate temperature control is necessary.

Influence of the quality of isoamyl alcohol

Because *iso*amyl alcohol obtained from fermentation, depending on its origin, can show variations with regard to its composition, we have investigated whether these differences influence the extinction coefficient. It did not appear to be the case for three distilled alcohols of different origin, b.p. 129-132° C.

However in some tests made with not freshly distilled *iso*amyl alcohol, fading of the color occurred. Therefore commercial *iso*amyl alcohol must always be distilled before use.

Excess reagent

Several tests were carried out in which the concentrations of the reagent were 0.02, 0.04, 0.06 and 0.08%, respectively.

No appreciable change in extinction coefficient was observed.

Validity of Beer's law

We have been able to prove that Beer's law is valid to the highest concentration used, namely 40 μg Cu/ml. The extinction is, however, very high for this concentration and gives a great error. For this reason the maximum concentration has been limited to 10 μg Cu/ml.

Setting up of calibration curves

Two methods were applied.

In the first method the complex is completely withdrawn from the aqueous layer by repeated extraction, whereupon the solution is made up to a definite volume.

Procedure: 50 ml solution containing 1-10 μg copper per ml were placed in a separating funnel. Some hydroxylaminechlorhydrate crystals were added to reduce Cu(II) to Cu(I) and the copper was extracted once with 20 ml *iso*amyl alcohol containing 0.02% cuproine and three times with 10 ml. The mixture was shaken each time for three minutes.

The third portion is practically colourless. The first three portions are collected in a 50 ml graduated flask and made up to 50 ml using the last portion. The extinction is measured against a blank with a Beckman DU spectrophotometer at 546 mμ, in Corex cells of 1,000 cm. A cell correction is eventually applied. The results are given in Table I.

TABLE I

μg Cu/ml	E	k	$\triangle k$
1	0.099	99.0	+ 1.1
2	0.193	96.5	— 1.4
3	0.296	98.7	+ 0.8
4	0.397	99.2	+ 1.3
5	0.490	98.0	+ 0.1
6	0.586	97.6	— 0.3
7	0.680	97.1	— 0.8
8	0.773	96.6	— 1.3
9	0.888	98.6	+ 0.7
10	0.979	97.9	0.0

Mean extinction coefficient $k = 97.92$

Mean square error for one measurement

$$\sqrt{\frac{\Sigma\,(\triangle\,k)^2}{n\text{-}1}} = 0.97 \text{ or } 0.99\%$$

The second method is an empirical one.

It has appeared from systematic investigation that the partition coefficient is very favourable and that after a short shaking time practically all the copper passes into the alcoholic layer. Therefore, besides the classical method based on repeated extraction, an empirical method was developed starting from a 50 ml solution that, under standard conditions, is only shaken once with 5 ml *iso*amyl alcohol. Against the slight loss of Cu (0.9%), there is at least a tenfold increase in sensitivity on account of the tenfold concentration. Moreover this method makes possible a more rapid determination of copper in materials of diverging origin, because the preliminary treatment of the sample can take place without any difficulty.

Procedure: In shaking flasks of 50 ml (Fig. 2) amounts of copper varying from 2.5 to 30 μg are made up to suitable dilutions. 1 ml conc. sulphuric acid, 2 ml 50% tartaric acid and 2 ml 15% hydroxylaminechlorhydrate are added. The solution is neutralised with 30% sodium hydroxide, added from a burette, to a pH 4-7, for which an external universal indicator is used.

After dilution to 50 ml a salt concentration is obtained in the aqueous layer that is comparable with that obtained after destruction of a plant sample, of blood, etc.

The flask is now placed in a thermostat at 25° C for 10 min. This temperature was chosen because it is nearest to normal room temperature in our laboratory.

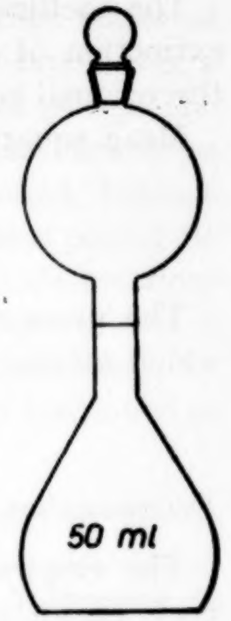

Fig. 2. Extraction flask

After the temperature has become constant, 5 ml *iso*amyl alcohol, containing 0.02% cuproine, are added and the flask shaken vigorously for 3 min. Errors can occur when temperature during shaking changes notably, on account of variation of solubility and of turbidity of the alcoholic phase at low temperatures.

After the separation of the alcoholic layer it is centrifuged for 1 min to free it from suspended droplets of water. The extinction of the clear purple solution is then measured at $\lambda = 546$ mμ against a blank to compensate for the copper content of the reagents and of the double distilled water.

The instrument used was a Beckman DU spectrophotometer.

Table II gives the results obtained for copper contents of 2.5 to 30 μg/50 ml.

TABLE II

μg Cu/50 ml	*E*	*k'*	Δ*k'*
2.5	0.059	1180	19
5.0	0.115	1150	—11
7.5	0.176	1182	—11
10.0	0.231	1158	—3
12.5	0.292	1165	—4
15.0	0.345	1150	1
20.0	0.462	1155	—6
25.0	0.587	1174	13
30.0	0.691	1151	—10

Mean extinction coefficient: $k' = 10.455/9 = 1161$

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The coefficient k' is the apparent extinction coefficient calculated from the extinction of the concentrated alcoholic phase and the concentration of Cu in the original solution.

Mean square error for one measurement:

$$\sqrt{\frac{\Sigma\,(\triangle\,k)^2}{n\text{-}1}} = 11 \text{ or } 0.95\%.$$

The mean square error is of the same order as for the classical method, which means that the empirical method is justified.

APPLICATIONS

Determination of copper in plants

The empirical method has been applied for the determination of Cu in sugar beet, grown by aquiculture at the "Centre pour l'amélioration de la betterave sucrière" at Tienen. Different parts of the sugar beet were used. These parts were first dried by infrared radiation at a temperature below 70°. They were then pulverised until everything could pass through a No. 100 sieve, and further dried at 105°. Constant weight was never reached, so that a well-defined procedure had to be followed accurately. The dried material, which is hygroscopic, is kept in sealed tubes. The organic material now has to be destroyed, for which a wet or dry method can be used.

1. *Destruction by dry method*

0.250 to 0.500 g plant material are weighed out in a porcelain crucible. The material is burnt for 24 h at a temperature below 450° C in order to prevent the melting of the ash. The inorganic residue is treated with 5 ml 6*N* hydrochloric acid and is heated on a waterbath until the carbonates and oxides have been dissolved. If there are still black carbon particles present, the solution is evaporated to dryness and burnt again for 2 [illegible] after which 5 ml 6*N* hydrochloric acid are added. After the dissolving of the [illegible]ides and carbonates, the insoluble silica residue is filtered off, washed, and the filtrate placed in a 50 ml shaking flask. This silica residue does not contain any copper that can be detected qualitatively. 2 ml 50% tartaric acid solution are added to the filtrate to keep the iron in solution. After this the procedure of the empirical method was used.

2. *Destruction by wet method*

0.250 to 0.500 g dry plant powder are weighed out in a pyrex destruction flask for micro-Kjeldahl determination according to PARNAS. 5 ml of a mixture of 1 part sulphuric acid (98%), 1 part perchloric acid (70%) and 3 parts nitric acid (66%) are added. The acids were redistilled to free them from traces of copper and then mixed in the given proportion. The mixture is heated over a micro-flame and the arising vapours are drawn off with a water-jet pump. The consecutive actions of the nitric, perchloric and sulphuric acid can clearly be followed. Danger of explosion through overheating is not to be feared, because the boiling point of sulphuric acid is much higher and the excess perchloric acid distils off, leaving the sulphuric acid in the flask. About 500 destructions following this method were carried out without any hitch. The residue is cooled off, diluted with a little water and washed into an extraction flask.

2 ml 50% tartaric acid solution are added and the treatment is continued as for the empirical method. Some results are given in Table III.

TABLE III

Sample		Extinction		µg Cu/ml	Difference %
No.	nature	dry method	wet method		
3697	lamina	0.585	0.586	110	0.17
3717	id.	0.566	0.567	107	0.27
3727	id.	0.381	0.380	72	0.26
3729	leaf whorl	0.217	0.222	42	2.2
3731	id.	0.143	0.137	27	4.2
3737	lamina	0.260	0.267	51	2.8
3741	id.	0.235	0.240	47	2.1
3743	root	0.287	0.290	55	0.9

The agreement between the results obtained by destruction by the dry method and by the wet method is satisfactory, since the mean difference is only of the order of 1.6%.

Determination of copper in water

For the "Centre pour l'amélioration de la betterave sucrière", the determination of copper in water used for aquiculture has been carried out.

Starting with 100 ml water shaken with 10 ml *iso*amyl alcohol containing 0.01% cuproine, up to 0.02 µg copper per ml could be determined. The determination of traces of copper in industrial and natural water is now carried on by the "Centre Belge d'Etude et de Documentation des Eaux".

Animal tissues and blood plasma

The determination of traces of copper in animal tissue proceeds according to the method used for plant material, with, nevertheless, this difference, that the destruction by the dry method is practically unworkable and leads to unreproducible results. The tissues are, therefore, treated without preliminary drying. Thus it is necessary to take ± 5 g samples of tissue and 5 ml of blood plasma. The destruction of these samples is carried out with the same mixture of acids. Some results obtained with different tissues are given in Table IV.

In collaboration with G. VERDONK, W. DANSERCOER AND Y. VAN MOFFAERT more than 200 blood plasmas obtained from normal and anaemic persons (men and women) were analysed to fix the mean copper content, about which very diverging data are given in the literature. The average results are given in Table V.

TABLE IV

Nature	Weight	Extinction/g	μg Cu/g
Kidney	3.864 g	0.105	4.5
Spleen	3.687	0.024	1.0
Lung	5.048	0.038	1.6
Heart	5.014	0.064	2.8
Liver	2.473	0.256	11.0

TABLE V

Nature	Number of determinations	average No. red blood corpuscles	Average Cu (μg / 100 g)
Normal men	66	4,520,000	107
Normal women	87	4,210,000	118
Anaemic men	14	3,540,000	123
Anaemic women	42	3,530,000	128

The clinical meaning of these data will be fully discussed elsewhere.

ACKNOWLEDGEMENT

The authors wish to thank W. DANSERCOER, E. FERNANDEZ-CALDAZ, A. HEIREMANS AND Y. VAN MOFFAERT for the care with which they have analysed numerous samples of plants and blood.

The determination of traces of copper in lamp-black

Determination of traces of copper and manganese in lamp-black is important for the rubber industry, since the content of these elements should be very low.

Procedure: 5 g lamp-black are weighed out in a porcelain crucible and burnt in an electric oven at 850°. The remaining oxides and carbonates are dissolved in 5 ml 6*N* hydrochloric acid (heated on a water bath). The insoluble silica residue is filtered off, and the filtrate is collected in a pyrex flask and made up to 50 ml. With a dry pipette 25 ml are now transferred to a 50 ml shaking flask and these are treated according to the empirical method. In the remaining 25 ml manganese can be determined spectrophotometrically after oxidation with periodate. This method allows the determination of copper up to 10^{-4} % and manganese up to 5.10^{-4} %.

The determination of traces of copper in steel

All colorimetric methods proposed up to now for determining traces of copper in steel up to 0.01% are only applicable to steels with a low content of alloy constituents.

The methods using diethylcarbamate and benzoinoxime are, among others, useless for Ni/Cr 18/8 steel so that their applicability is limited.

On the contrary the specificity of cuproine permits determination in these cases, without preliminary separation, as it appeared from the analysis of two synthetic steel solutions, in which the copper content varied between 0.1 and 0.01%.

Procedure: The following general method can be used for steel. 0.05 g steel are dissolved in a usual quantity of acid. After dissolving, 1 g tartaric acid and 2 ml 15% hydroxylaminechlorhydrate are added and the solution is neutralised with 30% sodium hydroxide to pH 4-7. The solution is then poured into an extraction flask (Fig. 2) and treated further according to the empirical method.

The usefulness of the method was tested by means of two synthetic steel solutions, made with the salts given in Table VI where the composition of the corresponding steels is also given.

TABLE VI

Element	Ni/Cr steel	Co steel	Salts used
Ni	8%	—	$Ni(NO_3)_2.6$ aq.
Cr	18%	4.5	$CrCl_3$. 6 aq.
Mn	2	0.4	$MnSO_4$. 4 aq.
Ti	0.5	—	$TiCl_3$ sol. 15%
Mo	2.5	0.9	Na_2MoO_4. 2 aq.
Co	—	13	$Co(NO_3)_2$. 6 aq.
V	—	1.5	$NaVO_3$. 4 aq.
W	—	18	Na_2WO_4. 2 aq.
Fe	69	60.7	$FeCl_3$. 6 aq.

These synthetic steel solutions, to which copper was added, were measured against a blank without copper, so that the copper content of the reagents was compensated. The results obtained after the addition of copper corresponding to a content of 0.01, 0.02, 0.05, and 0.1% in steel are given in Table VII.

TABLE VII

% Cu	Ni/Cr Steel		Co steel	
	% Cu found	% error	% Cu found	% error
0.01	0.01014	1.4	0.0096	4.0
0.02	0.0196	2.0	0.0199	0.5
0.05	0.0487	0.3	0.0495	1.0
0.1	0.1010	1.0	0.1024	2.4

References p. 274.

SUMMARY

A study is devoted to the spectrophotometric determination of traces of copper with cuproine as reagent. After having determined the absorption spectrum of the complex, the authors have studied successively the partition coefficient water/*iso*amyl alcohol; the stability of the complex (colour); the influence of some factors: pH, foreign ions, temperature, the quality of *iso*amyl alcohol, excess reagent; and the validity of Beer's law. Two different calibration curves were determined, one based on complete extraction of the complex and the other based on an empirical method, which is very rapid. In both cases the mean square error is less than 1%.

Finally, analysis methods were worked out for the determination of traces of copper in plants, animal tissues and blood, in water, in lamp-black and in steel.

RÉSUMÉ

Une étude est effectuée sur le dosage spectrophotométrique de traces de cuivre, au moyen de cuproïne comme réactif. Après avoir déterminé le spectre d'absorption du complexe, les auteurs ont examiné successivement le coefficient de partage eau/alcool *iso*amylique; la stabilité du complexe (coloration); l'influence du pH, des ions étrangers, de la température, de la qualité de l'alcool *iso*amylique, de l'excès de réactif; ainsi que la validité de la loi de Beer. Deux courbes d'étalonnage ont été tracées, l'une après extraction totale du complexe, l'autre basée sur une méthode empirique très rapide. Dans les deux cas, l'erreur moyenne est inférieure à 1%. Enfin, des méthodes ont été mises au point pour le dosage de traces de cuivre dans les plantes, dans l'eau, les tissus animaux et le sang, dans le noir de fumée et l'acier.

ZUSAMMENFASSUNG

Es wird eine Methode für die spektrophotometrische Bestimmung von Spuren Kupfer mit Cuproin als Reagenz beschrieben. Nach der Bestimmung des Absorptionsspektrums des Komplexes untersuchten die Autoren weiterhin den Verteilungskoeffizienten in Wasser/*iso*Amylalkohol, die Beständigkeit des Komplexes (die Farbe); den Einfluss des pH-Wertes, der fremden Ionen, der Temperatur, der Qualität des *iso*Amylalkohols, des Überschusses an Reagenz; und die Gültigkeit des Beer'schen Gesetzes. Zwei verschiedene Eichkurven wurden bestimmt, eine durch die vollständige Extraktion des Komplexes und die andere mit einer sehr rasch vor sich gehenden empirischen Methode. In beiden Fällen ist der mittlere quadratische Fehler geringer als 1%.

Schliesslich wurden Analysenmethoden zur Bestimmung von Spuren Kupfer in Pflanzen, in Wasser, tierischen Geweben und Blut, in Lampenruss und Stahl ausgearbeitet.

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THE MICRO-ESTIMATION OF COBALT WITH TRIPHENYLMETHYLARSONIUM THIOCYANATE

by

K. W. ELLIS AND N. A. GIBSON

Chemistry School, Sydney University, Sydney, N.S.W. (*Australia*)

INTRODUCTION

Triphenylmethylarsonium thiocyanate, in conjunction with an extraction technique, has already been shown to be useful for the colorimetric estimation of micro-quantities of iron[1] and the micro-detection of cobalt[2], and in this paper its use for the colorimetric micro-estimation of cobalt is examined.

Probably the most widely used general method of colorimetric estimation of cobalt, due originally to VOGEL[3], depends on the formation of the blue $[Co(CNS)_4]^{-2}$ complex anion, usually as the ammonium salt. Various methods of intensifying the colour have been suggested, principally either the addition of ethyl alcohol or acetone[4,5,6] or the extraction with solvents, such as amyl alcohol/ether mixtures[7,8,9]. In the former class, interference by iron and copper is serious, and, as well, the intensity of colour is dependent on the amount of thiocyanate and organic solvent present. In the extraction methods, interference by other metals is greatly reduced, but the high volatility of the solvents used makes accurate work difficult. In a recent modification[10], the tetraphenylarsonium salt is extracted with chloroform. This cation forms water-insoluble, chloroform-soluble salts with a large number of anions[11], and further is more difficult to prepare than the triphenylmethylarsonium cation. Chloroform is generally unsuitable as a solvent because of its high volatility.

DISCUSSION

The estimation of cobalt with triphenylmethylarsonium thiocyanate, as described in this paper, is subject to interference by coloured complex salts formed by iron (III), copper (II) and molybdenum (V), but this may be readily eliminated, as shown later. Nickel and manganese do not interfere.

The triphenylmethylarsonium radical is much more selective than the tetraphenylarsonium, and does not form water-insoluble compounds with, for instance, iodide and molybdate ions. Thus there is much less possibility of the arsonium radical being reduced below the concentration required in the water layer. The depth of colour developed is virtually independent of the amounts of triphenylmethylarsonium chloride and ammonium thiocyanate added, provided the aqueous layer is saturated with the arsonium thiocyanate.

The proposed solvent, *o*-dichlorbenzene (b.p. 180-183° C) has a far lower volatility than chloroform, and hence possible errors due to evaporation are minimised.

The absorption curve of the solution, whether in *o*-dichlorbenzene or ethylene dichloride, has a sharp absorption maximum at 627 mμ, with a small subsidiary peak at 590 mμ. This appears to be characteristic of the $[Co(CNS)_4]^{-2}$ complex, being independent of the cation or the solvent[11,12].

The isolation of the solid complexes $[R_4As]_2[Co(CNS)_4]$ has been described previously[2]. There is no evidence for the existence of the anion $[Co(CNS)_6]^{-4}$ in the solid state. Solutions prepared by dissolving $[Ph_3MeAs]_2[Co(CNS)_4]$ in *o*-dichlorbenzene show the characteristic maxima at 627 and 590 mμ, and no change occurs when excess of $Ph_3MeAsCNS$, which is also soluble in *o*-dichlorbenzene, is added. This leads to the belief that in contradiction to WEST AND DE VRIES[13], the anion $[Co(CNS)_6]^{-4}$ does not exist in solution.

The method is capable of determining from 10 to 100 μg of cobalt per ml with an accuracy of ± 2%. This accuracy can be maintained in the presence of large quantities of nickel and manganese without modification or separation, and after addition of suitable reagents, but without separation, in the presence of large amounts of copper, iron and molybdenum. Test solutions within the pH range of 1 to 4 are satisfactory.

The solution obeys Beer's Law over most of the suggested concentration range, deviating slightly close to the upper limit.

The stability of colour of the solution was excellent. Less than 1% fading occurred in 24 hours under ordinary laboratory conditions.

PROCEDURE

In a small separating funnel put *o*-dichlorbenzene (b.p. 180° to 183° C) (5 ml), then pipette in 10 ml of cobalt solution, which should contain between 10 and 100 μg of cobalt per ml and have a pH of 1 to 4. To this add 1 ml of 2% triphenylmethylarsonium chloride solution and 1 ml of 25% ammonium thiocyanate solution. Shake out arsonium thiocyanato-cobaltate (II) with *o*-dichlorbenzene and filter through a No. 2 sintered-glass filter. Extract the aqueous layer with a further 1 ml of *o*-dichlorbenzene. To the aqueous layer add 1 ml of 2% triphenylmethylarsonium chloride solution and extract twice with 1 ml of *o*-dichlorbenzene. Repeat this once more, then wash combined filtered extracts into a 25 ml graduated flask, make up to the mark, and compare with a blank solution in a "Spekker" photoabsorptiometer, using 1.0 cm cells, heat absorption filters H503 and orange-

red spectrum filters 607. Obtain cobalt content of solution by reference to a calibration curve prepared by treating a series of known solutions of cobalt in the same manner as above.

RESULTS

Results obtained over the whole range suggested are shown in Table I, the average mean deviation being less than 1%, and the maximum deviation in no case exceeding 2%.

TABLE I

SAMPLES (10 ml) CONTAINING 10 TO 100 μg OF COBALT PER ml

Cobalt used (μg ml)	Cobalt found (μg ml) Minimum	Cobalt found (μg ml) Maximum	Mean deviation (μg/ml)	Mean deviation (%)
10.0	9.9	10.1	0.1	1.0
20.0	19.75	20.25	0.25	1.25
30.0	29.5	30.5	0.3	1.0
40.0	39.5	40.5	0.5	1.25
50.0	49.5	51.0	0.75	1.5
60.0	59.5	60.5	0.5	0.8
70.0	69.5	70.5	0.5	0.7
80.0	80.0	80.0	0.0	0.0
90.0	90.0	90.0	0.0	0.0
100.0	100.0	100.0	0.0	0.0

TABLE II

Salt	%Co Calc.	Sample	%Co Found	Mean %Co. Found	Deviation from mean for sample	% Deviation from mean for sample
A	18.26	(i)	18.2	18.25	0.05	0.3
			18.3		0.05	0.3
		(ii)	18.4	18.4	0.00	0.0
			18.4		0.00	0.0
B	16.34	(i)	16.2	16.25	0.05	0.3
			16.3		0.05	0.3
		(ii)	16.2	16.25	0.05	0.3
			16.3		0.05	0.3
$[Co(NH_3)_6]Cl_3$	22.04	(i)	21.8	21.85	0.05	0.2
			21.9		0.05	0.2
		(ii)	22.3	22.2	0.1	0.4
			22.1		0.1	0.4

At the request of another member of the staff of the Chemistry School, analyses were undertaken of two forms of Vortmann's Salt, together with cobaltic hexammine chloride. The latter was used as check test on a salt of well-known composition. In each case, two samples of the salt were weighed out, fumed down with sulphuric acid, transferred to a graduated flask, made up to the mark with distilled water, and aliquots pipetted off for the colorimetric estimation. It will be noted from Table II that deviations in the colorimetric part of the analysis are smaller than those due to the rest of the operations.

INTERFERENCE

Anions. Sulphate, nitrate and chloride ions could all be present up to a concentration of 2*N* at pH 4. Tolerance to fluoride ions was rather higher, and to thiosulphate ions about the same, but phosphate could only be present up to a concentration of *N*/20. Nitric, hydrochloric and sulphuric acids caused an increase of cobalt estimated of more than 2% when present in concentrations greater than *N*/10. These results are summarised in Table III.

TABLE III

INTERFERENCE BY IONS ADDED TO 1000 μg OF COBALT IN DISTILLED WATER

Concentration of Added Reagent	Cobalt found after addition of -							
	H_2SO_4 (μg)	HCl (μg)	HNO_3 (μg)	$(NH)_2SO_4$ (μg)	NH_4Cl (μg)	NH_4NO_3 μg)	NaF (μg)	$Na_2S_2O_3$ (μg)
5*N*							1010	
2*N*	1100	1100	1100	1015	1020	1015	1005	
N	1250	1100	1100	1005	1005	1005	995	1000
N/10	1005	1015	1005					

Cations. The interference caused by the presence of other cations was determined by introducing them into a standard solution of cobalt containing 100 μg per ml. The results are shown in Table IV for concentrations causing a variation of 2% of the cobalt estimated.

The high tolerance to nickel is important, as cobalt and nickel usually occur as impurities in each other. The interference due to iron (III) can be eliminated by the addition of sodium fluoride to the test solution before the determination is carried out. Chromium (III) interferes only when present in amounts in excess of ten times that of the cobalt, so that when large amounts of chromium are present, a simple partial separation will reduce it to a safe limit. The interference of copper (II) can be eliminated by the addition of sodium thiosulphate if the copper

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TABLE IV

Metal	Interfering Concentration	Reading too high (+) or too low (—)	X Co Concentration
Ni	10,000 μg/ml	+	100
Mn	10,000 μg/ml	+	100
Cr	1,000 μg/ml	—	10
Mo(V)	5 μg/ml	+	0.05
Fe(III)	5 μg/ml	+	0.05
(Fe(III) (+ 5*N* NaF)	10,000 μg/ml	+	100
Cu(II)	5 μg/ml	+	0.05
Cu(II) (+ 5*N* $Na_2S_2O_3$)	1,000 μg/ml	—	10

is present in amounts less than ten times that of the cobalt. If present in greater concentrations, it can either be decreased below this limit by a simple partial separation, or the interference suppressed by reduction to copper (I) with potassium iodide, followed by the addition of sodium thiosulphate to reduce iodine formed[10]. Molybdenum (V) also interferes seriously, but this can be easily overcome by either reduction or oxidation of the molybdenum.

SUMMARY

Triphenylmethylarsonium thiocyanate is recommended for the colorimetric micro-estimation of cobalt. The procedure is suitable within a range of 10 to 100 μg of cobalt per ml with an accuracy of about 2%. It enables the micro-estimation of cobalt to be carried out on most of its common alloys, no prior separation being required in most cases, and in the others, simple partial separations being sufficient.

RÉSUMÉ

Le thiocyanate de triphénylméthylarsonium est recommandé pour les microdosages colorimétriques du cobalt. Ce procédé permet de doser des teneurs de 10 à 100 μg de cobalt par ml, avec une précision d'environ 2%. On peut ainsi effectuer des microdosages de cobalt dans la plupart de ses alliages courants. Généralement une séparation préalable n'est pas nécessaire, éventuellement une séparation partielle est suffisante.

ZUSAMMENFASSUNG

Triphenylmethylarsoniumthiocyanat wird zur kolorimetrischen Mikrobestimmung des Kobalts empfohlen. Das Verfahren ist in einem Bereich von 10-100 μg Kobalt pro ml mit einer Genauigkeit von 2% anwendbar. Es ermöglicht die Mikrobestimmung des Kobalts in den meisten seiner gebräuchlichen Legierungen anzuwenden, ohne in den meisten Fällen eine vorherige Abtrennung zu erfordern, oder in anderen Fällen bei denen eine einfache teilweise Abtrennung genügt.

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HETEROMETRIC MICROTITRATION OF NICKEL WITH DIMETHYLGLYOXIME

by

M. BOBTELSKY AND Y. WELWART

Department of Inorganic and Analytical Chemistry of the Hebrew University, Jerusalem (Israël)

The determination of nickel with dimethylglyoxime is the most frequently used method for precipitation of nickel. A great deal of work has been done in order to determine nickel in alloys in which nickel is the major or minor component. We present here a method which is easy to carry out and which requires a minimum time (5-10 minutes) for a complete heterometric titration (after some experience with heterometric titrations). On the basis of the material accumulated by us, we have established that the determination of nickel can be made in all practical cases where nickel is a component with other metals in any given alloy. By using an appropriate metal complex binder we could precipitate nickel without any interference from other metals.

We present here a small fraction of the titrations made, in order to give a conception of the method, its efficiency and the results obtained. The results of titrations of micro quantities of nickel in the presence of other metals will be presented in further reports.

As Table I and the Figures 2-3 show, 0.5-3.0 mg nickel in 20 ml solution can be titrated with dimethylglyoxime dissolved in ethyl alcohol. The errors amount to one hundredth of a mg and theoretical results are mostly obtained.

REMARKS

The method presented can be used either for microdetermination of nickel with dimethylglyoxime or for microdetermination of dimethylglyoxime with a nickel solution. Both can be determined with the same accuracy. This method can be used for the standardisation of the alcoholic dimethylglyoxime solution. The latter can then be used for the determination of unknown nickel solutions. A water solution of a regular nickel salt in a concentration of $0.0005M$ or higher may be titrated with dimethylglyoxime, the concentration of which must be $0.01M$ or higher. Conversely, solutions of dimethylglyoxime of about $0.0005M$

or higher may be titrated with a 0.005*M* or higher nickel solution. (The percentage of alcohol in the titrated solution should be low.) The optical density values obtained depend of course on the diameter of the vessel used, that is, on the height of the layer used. In all cases we used a cylindric vessel of $\sim$3.8 cm diameter and so obtained an absorption layer of about 2.0 cm. The analysed solutions were buffered with NH_4Cl/NH_3 and the pH was about 9.5.

EXPERIMENTAL

The reagents used were either analytical reagents or chemically pure. The description of the "Heterometer" (= photoelectric titrimeter) and the heterometric titrations is given elsewhere[1]. A red filter was used in all titrations.

RESULTS

Fig. 1 presents the results of two parallel pH and heterometric titrations. The experiments were made in order to study the pH conditions necessary for a heterometric titration of nickel with dimethylglyoxime. The optical density curve shows that from pH 5.5-6.0 onwards, a quantitative precipitation of nickel-dimethylglyoxime occurs. In addition no precipitation is obtained below pH$\sim$4.0. No influence whatever of the rising pH's (between pH 6 and 11) on the density curve, could be detected.

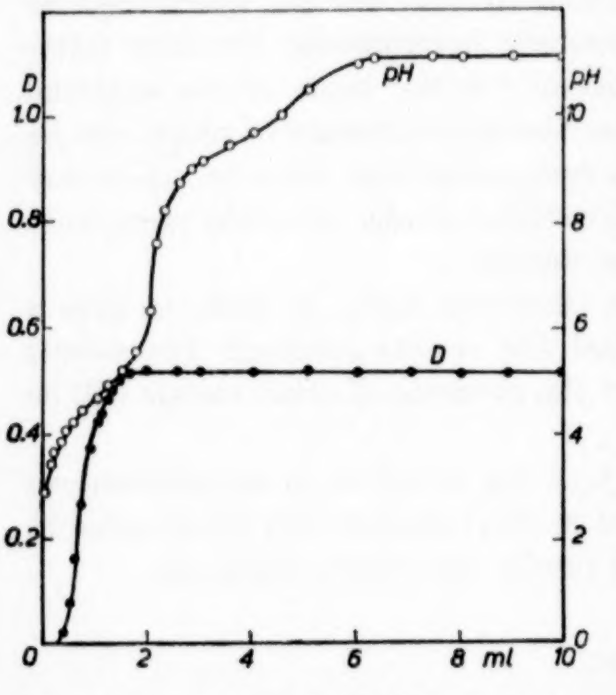

Fig. 1. 5 ml 0.002*M* $NiSO_4$ + 5 ml 0.005*M* dimethylglyoxime + 2 ml 1.0*M* CH_3COOH + 3 ml 1.0*M* NH_4NO_3 + 5 ml H_2O + *x* ml 1.0*M* NaOH.

Table I and Figures 2 and 3 give a compilation of titrations of $NiSO_4$ solutions with dimethylglyoxime (exp. 1-7) and of titrations of dimethylglyoxime with $NiSO_4$ solutions (exp. 8-10). An 0.0005*M* Ni^{+2} solution may be titrated with 0.01*M* dimethylglyoxime (exp. 3). A theoretical value for nickel is obtained. The same titration (exp. 2 and Fig. 2, curve 2) made with a *more* dilute dimethylglyoxime solution gives a lower maximum optical value and the determination can no longer be made with sufficient certainty. On the other hand, as exp. 1 shows, a $NiSO_4$ solution of a much higher nickel content can be titrated with an 0.05*M* dimethylglyoxime solution and here too (although the maximum optical density value is very high) theoretical results are obtained. It is interesting

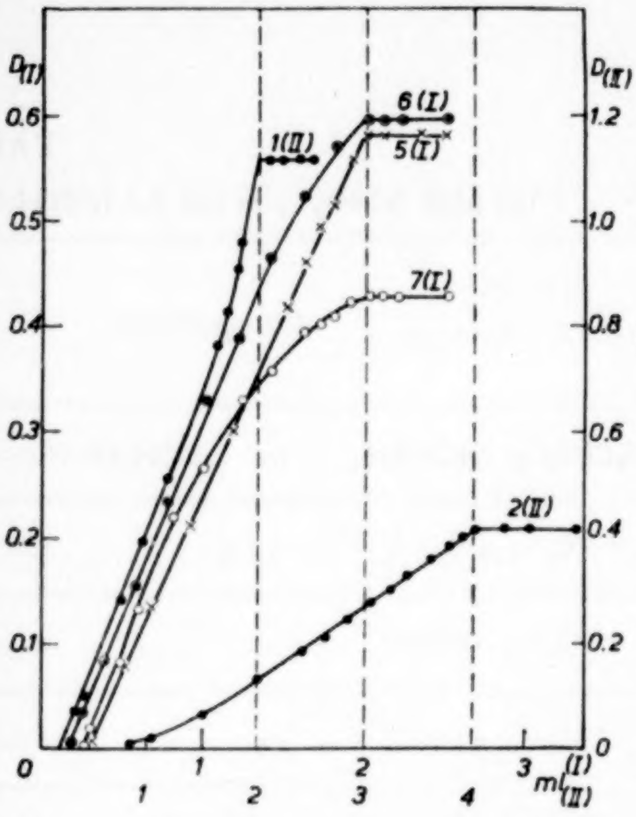

Fig. 2. Titration curves of nickel with dimethylglyoxime.

to learn that reverse titrations can be made with almost the same results (exp. 8-10 and Fig. 3). The latter may be used for a precise titration of micro quantities of dimethylglyoxime. In exp. 8, the error is less than 1% and in exp. 9, a theoretical value is obtained. In extremely dilute solutions of dimethylglyoxime the results become less certain. In all the three last cases, the maximum optical density values obtained are almost proportional to the concentration of dimethylglyoxime measured. Exp. 6 and 7 were made with the purpose of studying the influence of of supplementary metal complex binders, which were later used by us for microtitrations of nickel in the presence of other metals. It can be seen that the presence of even a 50 fold concentration of sodium tartrate or $Na_5P_3O_{10}$ has no influence on the results obtained. In the above cases, the titration took no more time than in the absence of supplements. The influence of the addition of a large quantity of alcohol (= 50% alcohol), was studied, (exp. 7). In contrast to all the other titrations, in this last case the titration took 45 minutes and the accuracy was no longer good.

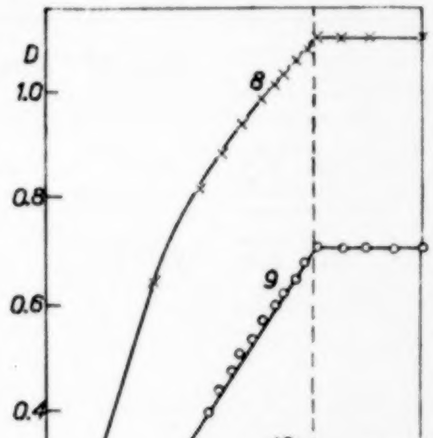

Fig. 3. Titration curves of dimethylglyoxime with nickel.

METHOD

General. The titrations are made at room temperature by a dropwise addition of dimethylglyoxime or nickel solution, from a microburet to the analysed solution, while the latter is stirred vigorously. The *first* optical maximum density point is obtained from the curve plotted by drawing a line through the maxima optical density points obtained, taking the first contact point.

Determination of nickel. To about 20 ml water solution of nickel which contains $\gtrsim$ 0.5 mg of nickel, are added one ml 2.0*M* NH_4Cl and 1.5 ml

TABLE I

GENERAL COMPOSITION: x ml mM $NiSO_4$ + a ml 1.0M NH_4Cl

Exp. No.	Composition
1	5 ml 0.01M $NiSO_4$ + 2 ml NH_4Cl + 3 ml NH_3 + 10 ml H_2O
2	5 ,, 0.002 ,, ,, + 1 ,, ,, + 1.5 ,, ,, + 12.5 ,, ,,
3	5 ,, 0.002 ,, ,, + 2 ,, ,, + 3 ,, ,, + 10 ,, ,,
4	5 ,, 0.001 ,, ,, + 1 ,, ,, + 1.5 ,, ,, + 15 ,, ,,
5	5 ,, 0.002 ,, ,, + 2 ,, ,, + 3 ,, ,, + 10 ,, 0.1M K_2Ta
6	5 ,, 0.002 ,, ,, + 2 ,, ,, + 3 ,, ,, + 5 ,, 0.1M $Na_5P_3O_{10}$
7	5 ,, 0.002 ,, ,, + 2 ,, ,, + 3 ,, ,, + 10 ,, alcohol
8	5 ,, 0.01M dimgl. + 2 ,, ,, + 3 ,, ,, + 10 ,, H_2O
9	2.5 ,, 0.01 ,, ,, + 1 ,, ,, + 1.5 ,, ,, + 15 ,, ,,
10	2.0 ,, 0.005 ,, ,, + 1 ,, ,, + 1.5 ,, ,, + 15.5 ,, ,,

+ *b* ml 1.0*M* NH_3 + *c* ml H_2O + *y* ml *nM* dimethylglyoxime. Volume = 20 ml.

	Ni mg		*x* =	Max.	error	
	content	found		optic. density	mg	γ/ml
x ml 0.05*M* dimgl.	2.9345	2.9345	2.0	1.11	0.0	0.0
x ,, 0.005 ,, ,,	0.5869	0.5869	4.0	0.31	0.0	0.0
x ,, 0.01 ,, ,,	0.5869	0.5869	2.0	0.43	0.0	0.0
x ,, 0.005 ,, ,,	0.2935	0.2935	2.0	0.17	0.0	0.0
x ,, 0.01 ,, ,,	0.5869	0.5860	1.98	0.58	—0.0009	—0.4
5 ,, H_2O + *x* ml 0.01*M* dimgl.	0.5869	0.5800	1.97	0.59	—0.0069	—0.3
x ,, 0.01*M* dimgl.	0.5869	0.5722	1.95	0.42	—0.0147	—0.7
x ,, 0.01 ,, $NiSO_4$	1.4692	1.4576	2.48	1.10	—0.0116	—0.5
x ,, 0.005 ,, ,,	0.7346	0.7346	2.5	0.71	0.0	0.0
x ,, 0.002 ,, ,,	0.2935	0.2911	2.48	0.31	—0.0024	—0.1

$2.0M$ NH_3 solution (pH ∿ 9.5). The titration is made with an alcoholic solution of $0.01M$ — $0.05M$ dimethylglyoxime. Error = 0-1%.

Determination of dimethylglyoxime. To about 20 ml water solution of dimethylglyoxime which contains $\geqq$ 1 mg of the latter, are added one ml $2.0M$ NH_4Cl and 1.5 ml $2.0M$ NH_3 (pH ∿ 9.5). The titration is made with an $0.01M$ — $0.005M$ $NiSO_4$ solution (or other nickel salt). The amount of alcohol added should not be great (see text). Error = 0-1%.

SUMMARY

A new "heterometric" method is presented for the microdetermination of nickel with dimethylglyoxime. $\geqq$ 0.5 mg of nickel in 20 ml of solution may be determined. The error lies between zero and 0.4 μg per ml. Solutions of dimethylglyoxime which contains $\geqq$ 1 mg dimethylglyoxime in 20 ml of solution may be determined with a nickel solution. The error lies between zero and 0.5 μg per ml. The time required for a titration at room temperature is 5-10 minutes.

RÉSUMÉ

Une nouvelle méthode ,,hétérométrique" est présentée pour la microdétermination du nickel avec la diméthylglyoxime. Selon cette méthode $\geqq$ 0.5 mg de nickel peuvent être déterminés, dans 20 ml de solution. L'erreur est comprise entre 0 et 0.4 μg/ml. Des solutions de diméthylglyoxime contenant $\geqq$ 1 mg de diméthylglyoxime (dans 20 ml de solution) peuvent être déterminées à l'aide d'une solution de nickel. L'erreur est comprise entre 0 et 0.5 μg per ml. Le temps nécessaire pour une titration est de 5-10 minutes à la température ordinaire.

ZUSAMMENFASSUNG

Eine neue ,,heterometrische" Methode zur Mikrobestimmung von Nickel mit Dimethylglyoxim wird presentiert. $\geqq$ 0.5 mg Nickel in 20 ml Lösung kann mit einem Fehler von null bis 0.4 Mikrogramm per ml bestimmt werden. Lösungen die $\geqq$ 1 mg Dimethylglyoxim in 20 ml enthalten können mit einer gestellten Nickelsalzlösung mit einem Fehler von etwa 0.5 Mikrogramm per ml bestimmt werden. Eine Titration dauert 5-10 Minuten.

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POLAROGRAPHIC REDUCTION OF GERMANIUM

by

A. K. DAS GUPTA AND C. K. N. NAIR

Division of Inorganic and Analytical Chemistry, National Chemical Laboratory, Poona-8 (India)

INTRODUCTION

In an earlier note[1], the authors reported having obtained polarographic reduction waves with tetravalent germanium under specified experimental conditions. Although the reducibility of tetravalent germanium at the dropping mercury electrode had been discounted by ALIMARIN AND IANOV-EMIN[2], we are presenting here data which show that clearly-defined polarograms with tetravalent germanium can be obtained both under acid and alkaline conditions. No attempt has been made in the present paper to go into a theoretical discussion of this reduction phenomenon or to derive the diffusion current constant of the element. These data, however, establish that tetravalent germanium is quantitatively reducible at the dropping mercury cathode. ALIMARIN AND IVANOV-EMIN[2], and COZZI AND VIVARELLI[3] have used the polarographic technique for the determination of germanium, but their procedure requires prior chemical reduction of tetravalent to divalent germanium by means of hypophosphorous acid.*

EXPERIMENTAL

A standard stock solution of tetravalent germanium was prepared from the pure dioxide obtained through the tetrachloride, by dissolving in water a weighed quantity of the oxide and making up to volume. Aliquots of this solution, which contained 120 ppm germanium, were suitably diluted in the presence of the requisite amounts of solutions of ammonium chloride, ammonium hydroxide and gelatin, so as to give a final concentration of materials indicated in the notes accompanying the figures presented. Polarographic measurements were made with a Tinsley Automatic Recording Polarograph at a temperature of 30° C with a stationary mercury pool anode. All curves were recorded at a drop rate of 2.8 seconds, and the average m-value was 1.62 mg/sec. The solutions were deoxygenated by bubbling nitrogen through them for 5-10 minutes.

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* VALENTA AND ZUMAN[4] have also reported recently the reducibility of Ge^{+4} in ammoniacal-ammonium chloride medium. They have noted only a single wave at — 1.4 V (*C.A.*, 46 (1952) 10953 f). Their failure to observe the second wave is apparently due to the low concentration of ammonium chloride used, a fact which is explained elsewhere in the present paper.

RESULTS AND DISCUSSION

Occurrence of germanium waves

It has been observed that no reduction wave of Ge^{+4} appears when the acidity of the solution is high. Even at a pH of 2.4 (Fig. 1a) no germanium wave is formed. This might account for the failure of ALIMARIN AND IVANOV-EMIN to observe the reduction waves of tetravalent germanium in acid solutions. Above pH 5 a single wave begins to appear, until at pH 10 the wave becomes well defined. The polarograms in Fig. 1 were taken with solutions, the pH of which was altered by the addition of drops of hydrochloric acid or ammonia, and which contained no indifferent electrolyte or maximum suppressor.

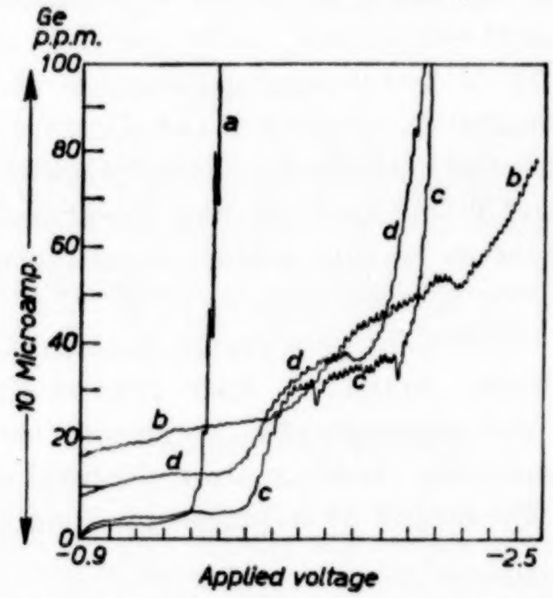


Fig. 1. Effect of pH on the reduction waves of tetravalent germanium (a) pH 2·4, (b) pH 6, (c) pH 7·5 (d) pH 10 (all polarograms with solutions containing 12 ppm Ge).

Ammonium chloride as supporting electrolyte

Figure 2 presents polarograms that show the effect of ammonium chloride both on wave heights and the half-wave potentials. While a progressively increasing concentration of ammonium chloride causes the formation of double waves, it also shifts the half-wave potentials to more positive values. Moderate increases in the concentration of ammonium chloride do not affect the wave heights, but a very large increase tends to increase the wave heights simultaneously (Fig. 2 c, d and e). A concentration of 0.1*M* ammonium chloride in solution with 0.5*M* ammonium hydroxide has been found to give very satisfactory polarograms.

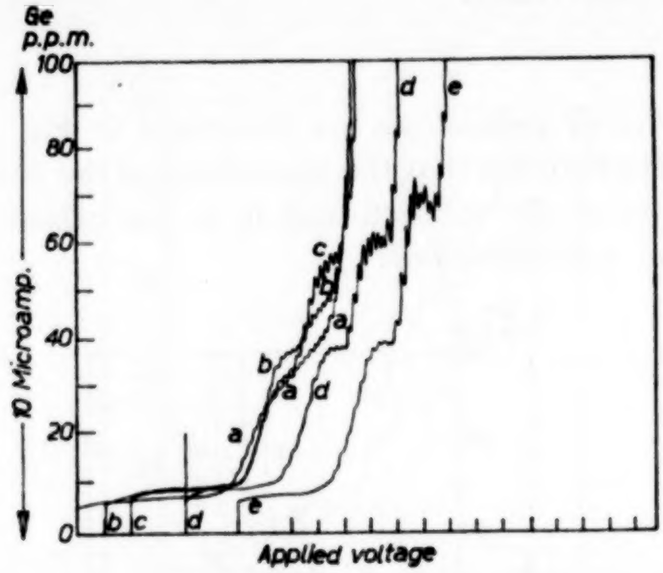
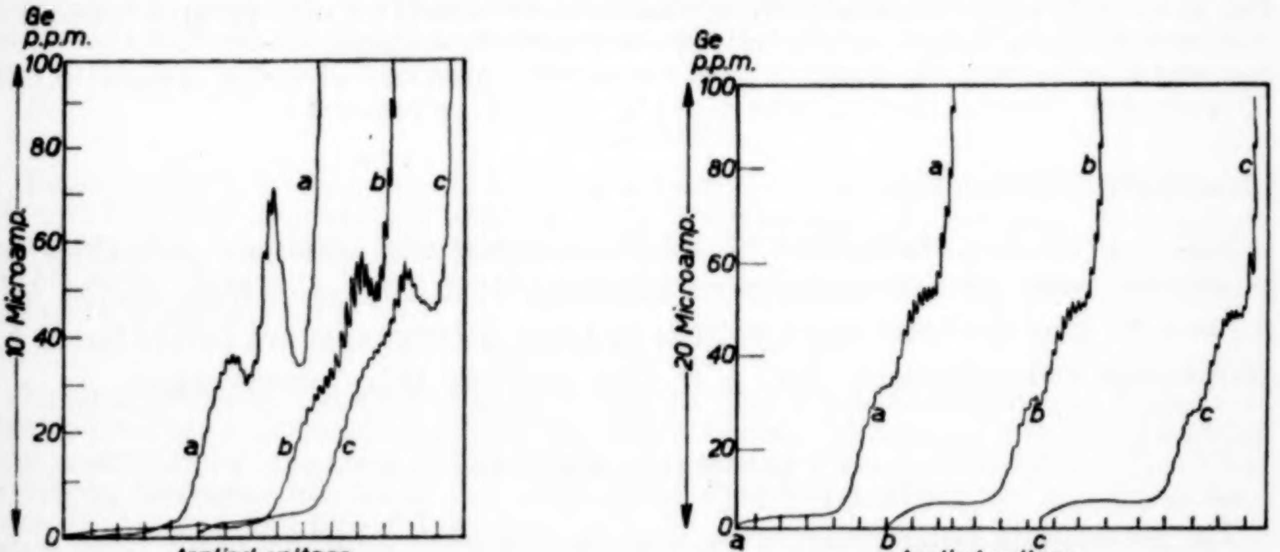


Fig. 2. Effect of ammonium chloride concentration on wave heights (a) No NH_4Cl (b) 0.02*M* NH_4Cl (c) 0.1*M* NH_4Cl (d) 0.5*M* NH_4Cl (e) 1*M* NH_4Cl. All solutions contained 12 ppm Ge; 0.01*M* Gelatin and 0.5*M* NH_4OH. Starting voltage — 1.0 V.

Gelatin as the suppressor of maxima

Fig. 3 (A and B) clearly show the effective manner in which gelatin suppresses the polarographic maxima of germanium waves. The polarograms presented in Fig. 3 B point to the fact that, by suitably altering the concentration of gelatin



A

B

Fig. 3. A. Effect of gelatin as the suppressor for the polarographic maxima of germanium waves (a) no gelatin (b) 0.01% gelatin (c) 0.005% gelatin (all solutions contained 12 ppm Ge, 0.02*M* NH_4Cl and 0.5*M* NH_4OH. Starting voltage —1.0 V).
Fig. 3. B. Polarograms of tetravalent germanium (a) 0.02% Gelatin (b) 0.03% Gelatin (c) 0.04% Gelatin (all solutions contained 20 ppm Ge, 1.0*M* NH_4Cl and 0.5*M* NH_4OH).

in the solution, the shape of the polarograms can be considerably improved. On the whole it has been observed that a concentration of gelatin equal to 0.01 per cent. is suitable in most cases.

Double waves

Some double waves of germanium are presented in Fig. 4. It was observed during the course of our studies that the appearance of the double waves is greatly dependent on the pH of the solution and to a less extent on the ammonium chloride and gelatin concentrations.

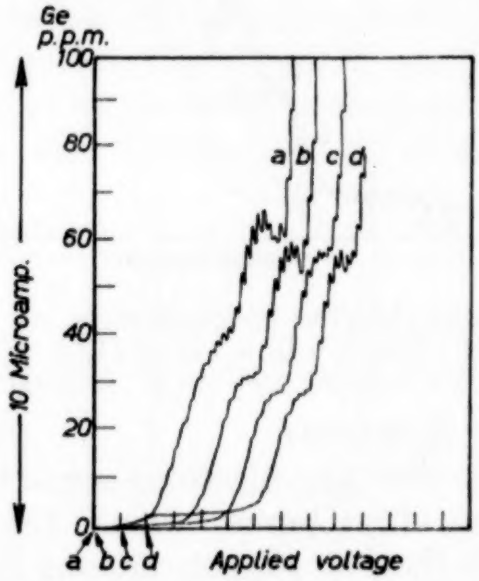


Fig. 4. Polarograms of tetravalent germanium a. (Starting V—1.1) 12 ppm Ge in the presence of 0.5M NH_4Cl, 0.5M NH_4OH and 0.005% Gelatin.
b, c and d. (Starting V—1.0) 12 ppm Ge in the presence of 0.5M NH_4Cl, 0.5M NH_4OH and 0.01%, 0.012% and 0.015% Gelatin respectively.

Quantitative relationships

Fig. 5 presents polarograms of solutions containing different quantities of germanium with all other conditions identical. It can be seen from curves (a), (b) and (c) that the total wave heights in these polarograms are proportional to germanium concentrations. Fig. 3 B also confirms these observations.

GENERAL COMMENTS

The germanium polarograms were reproducible with solutions made from pure germanium tetrachloride (Merck). The separation of the two waves into clearly identifiable components is merely a matter of adjustment of the concentration of ammonium chloride and ammonia. In solutions containing 1M ammonium chloride and 0.5M ammonia, the half-wave potential of the first wave is −1.45 V and that of the second wave −1.70 V. These potentials are, of course, variable with the concentration of the supporting electrolyte and maximum suppressor.

References p. 291.

ACKNOWLEDGEMENT

The authors are indebted to DR. J. GUPTA, Assistant Director, Division of Inorganic & Analytical Chemistry, for his interest in the work and for helpful suggestions and criticisms.

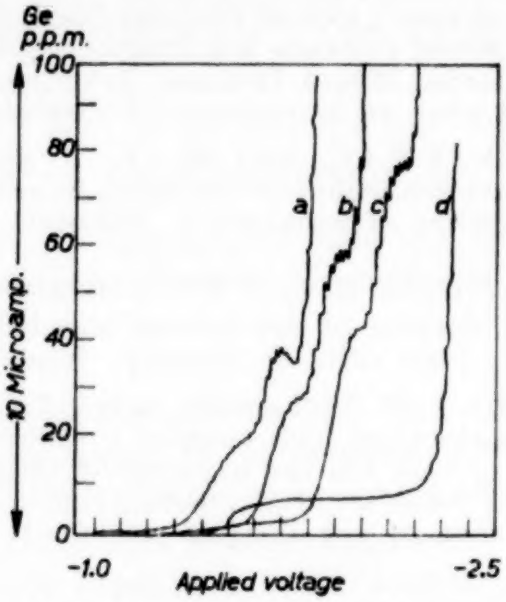


Fig. 5. Polarograms of tetravalent germanium (a) 7 ppm Ge (b) 12 ppm Ge (c) 15 ppm Ge (d) no Ge in the presence of $0.5M$ NH_4Cl, $0.5M$ NH_4OH and 0.015% Gelatin.

SUMMARY

In a previous note the authors had reported the polarographic reduction of tetravalent germanium. These observations were confirmed, and full data are presented here which show the two-step reduction of tetravalent germanium under the dropping mercury electrode, from ammoniacal-ammonium chloride solutions.

RÉSUMÉ

Faisant suite à une précédente note sur la réduction polarographique du germanium tétravalent, les auteurs confirment leurs observations et donnent les résultats obtenus. Les polarogrammes présentent les 2 paliers de réduction du germanium tétravalent (électrode à gouttes de mercure — solution de base: ammoniaque — chlorure d'ammonium).

ZUSAMMENFASSUNG

In einer früheren Veröffentlichung haben wir über die polarographische Reduktion des vierwertigen Germaniums berichtet. Diese Beobachtungen werden nun bestätigt and ausführliche Angaben gemacht. Sie zeigen eine Zweistufenreduktion des vierwertigen Germaniums unter der tropfenden Quecksilberelektrode aus einer Ammoniak-Ammoniumchlorid Lösung.

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SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the North of England Section

An Ordinary Meeting of the North of England Section of the Society of Public Analysts and Other Analytical chemists was held at 2 p.m. on Saturday, May 2nd, 1953, at the City Laboratories, Mount Pleasant, Liverpool 3. Mr. A. A. D. COMRIE, B.Sc., F.R.I.C., presided over an attendance of fifty-eight.

Mr. W. GORDON CAREY, F.R.I.C., and Mr. J. G. SHERRATT, B.Sc., F.R.I.C., introduced a comprehensive discussion on *The Analysis of Waters, Sewages and Effluents* to which a large number of members contributed.

Summer Meeting of the North of England Section

The Sixteenth Summer Meeting of the Section was held at the Imperial Hotel, Llandudno, from Friday, June 12th, to Monday, June 15th, 1953.

The Vice-Chairman, Mr. J. R. WALMSLEY, A.M.C.T., F.R.I.C., Ph.C., presided and thirty-eight members attended, including the President, Dr D. W. KENT-JONES, F.R.I.C., and Mrs. KENT-JONES. On the morning of Saturday, June 13th, a paper was presented by Mr C. A. ADAMS, C.B.E., B.Sc., F.R.I.C., on *Random Reflections on Food Legislation*. A tour of the district was made by motor coach on the Sunday afternoon.

Summary of paper on Random Reflections on Food Legislation

Mr. ADAMS said that the new Food and Drugs Bill now being drafted for presentation to Parliament was a matter of outstanding importance to Public Analysts and Chemists engaged in food manufacture, but it was also of importance to the general public, as buyers and consumers of food. On the interest shown by the general public much of the success of the Bill would depend, and it was to be hoped that members of the Society and the general public would do their utmost to stimulate this interest; for legislation seldom ran ahead of public opinion.

The outstanding interest in the new Bill would be in the powers sought to transfer temporary war-time legislation into permanent form and in any additional powers that might be necessary to deal with the addition of chemicals to food, whether intentional in the course of manufacture, or adventitious in the form of pesticide residues or in any other way. These matters had recently been the subject of official enquiry in the United States of America. They had also been dealt with at length by Dr. J. R. NICHOLLS in his recent presidential address and were summed up from the official angle by the Lord President of the Council in the Annual Report of the Advisory Council on Scientific Policy, a year ago.

Mr. ADAMS said that in his view the main value of a change in the law would be in relation to the use of chemicals newly introduced into the food industry.

If the Orders under the Defence (sale of Food) Regulations, 1943, were included in the new Bill, it would make them unalterable without appeal to Parliament. Instead, fuller powers to make such Orders would be sought in the Bill, and the Orders could then be re-enacted. Amongst these Orders the speaker allotted pride of place to the Labelling of Food Orders and the Food Standards Orders. All these Orders had been enforced by the Food and Drugs Authorities as though they were part of the Food and Drugs Act.

As the result of the experience in the working of these Authorities and food manufacturers, he was of the opinion that we had seen some welcome progress in what might be called the "Co-operative administration of food legislation".

If the range of the Food and Drugs Act was to be extended to cover problems arising from the use of chemicals, pesticide residues and the sale of sub-standard products, now was the time to make recommendations. Once the Bill became law, further changes might be long delayed.

ENHANCEMENT OF THE REDUCING PROPERTIES OF METALLIC MERCURY IN PRESENCE OF COMPLEX FORMING IONS*

by

F. BURRIEL-MARTÍ, F. LUCENA-CONDE AND S. BOLLE-TACCHEO

Laboratories of Analytical Chemistry of the Faculty of Science and the High Council of Scientific Research, Madrid (Spain)

Metallic mercury in a neutral or acid medium has only slight reducing properties unsuitable for analytical purposes. In the presence of ions forming precipitates or complexes with the mercuric or mercurous ions, however, this reducing power is enhanced. The classical example is the enhancement in the presence of hydrochloric acid, enabling ferric, vanadic and other ions to be reduced quantitatively. This reaction is the basis of certain methods for the determination of these ions. The main detraction of this reduction is the production of a precipitate of mercurous chloride, which yields a colloidal suspension with the metallic mercury, thus rendering the separation of the reduced solution a troublesome process.

Another possibility, which has not been hitherto exploited, is to enhance the reducing power of mercury in the presence of ions with which it forms stable complexes. The mercurous ion does not form any suitable complex, but the mercuric ion forms several, the most promising being those with thiocyanate and cyanide.

IN THE PRESENCE OF THIOCYANATE

In the presence of thiocyanate metallic mercury acts as a reductor according to the following reactions:

$$\mathrm{Hg} + 4\,\mathrm{SCN}^- \text{———} [\mathrm{Hg(SCN)_4}]^{-2} + 2\,\mathrm{e}$$
$$2\,\mathrm{Hg} + \mathrm{SCN}^- \text{———} \mathrm{Hg_2(SCN)_2} + 2\,\mathrm{e}$$

The former reaction is the most important, the latter only taking place if the thiocyanate concentration is rather small. A discussion concerning the influence of the thiocyanate concentration on the redox system of the ions of mercury and its stability has been developed fairly recently[1].

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* Read at the Symposium of Analytical Chemistry, Birmingham University, Sept. 11th and 12th, 1952.

The reducing power of mercury in presence of 0.1M thiocyanate is similar to that in the presence of hydrochloric acid; it is fairly independent of pH, since thiocyanic acid is a strong acid.

The most important reaction is the reduction of ferric ions. When the ferric thiocyanate complex is stirred with mercury in the presence of an excess of thiocyanate, it is quantitatively reduced to the ferrous state in a few seconds; at the end of this time the solution is quite colourless. The presence of air does not interfere. In this way it has advantages over zinc and cadmium amalgams, since with these the reduction of ferric ion is only complete in the absence of the air.

To explain the great speed of this reduction a *catalytic effect* of the thiocyanate ion cannot be excluded. A similar catalytic effect has been observed by some authors in the reduction of ferric ion with titanous[2] and uranous salts[3], and by the present authors in the reduction with sulphurous acid[4].

The effect of the thiocyanate concentration is of interest. When small amounts are present mercurous thiocyanate is precipitated. This usually interferes, but it can readily be avoided by increasing the thiocyanate concentration. In general, to reduce a 0.01M solution of ferric ion without forming a precipitate of mercurous thiocyanate, a concentration of at least 0.05M is required.

The amount of mercury dissolved corresponds exactly with the amount of ferric ion originally present. This shows the stoichiometry of the reaction and the absence of secondary reactions.

The most important analytical application of this reaction is for the reduction of ferric iron prior to titrimetric determination with potassium dichromate or ceric sulphate.

The advantages are as follows:

1. The reduction is very rapid.
2. Quantitative reduction is ensured, since the thiocyanate acts as an indicator and eliminates the errors due to incomplete reduction.
3. Ions with a low reducing power do not interfere.

The method has been applied to the determination of iron on the macro and semimicroscale, good results being obtained. In the titrimetric procedure the thiocyanate is masked with mercuric ions following a method previously described[5], and the titration is carried out with dichromate or ceric sulphate. The latter is particularly suitable on the semimicroscale and the potentiometric method can be used.

With this procedure the preparation of a reductor column is avoided. The reduced solution is easily separated from the mercury by decantation or addition of carbon tetrachloride, with an immiscible layer between the two liquids[6]. A special apparatus has been designed for working on the semimicroscale. The interference produced in high concentrations of hydrochloric acid is the principal disadvantage of the method.

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The action of the mercury-thiocyanate system on other oxidising substances has also been studied. Titanic and chromic salts are not reduced. The cupric ion is reduced in neutral or acid medium, yielding a grey precipitate of cuprous thiocyanate mixed with the mercury. The chromate ion is not reduced in neutral medium, while in acid medium it oxidises the thiocyanate. The vanadate ion is not reduced in neutral medium, but in acid medium the characteristic blue complex thiocyanate of trivalent vanadium is produced. In a similar way molybdate is not affected in neutral medium, while in acid medium it is reduced to the characteristic red complex. This reaction can be utilised in qualitative analysis for the detection of molybdate ion, instead of the classical reduction with stannous chloride. The ferricyanide ion is reduced to ferrocyanide in neutral, acid and alkaline medium.

On the other hand, the present authors think it is of interest to remark on the relations between these studies and those made fairly recently, on the properties of mercurous nitrate as a reductimetric reagent. In fact mercurous nitrate has been developed as a reagent for the determination of ferric iron[7], copper[8] and many other reducing or oxidising substances[9]. Therefore, in all titrimetric determinations with mercurous salts the reduction takes place not only by means of the mercurous ions but initially because there is a disproportion between the mercurous and thiocyanate ions so that it is the metallic mercury produced in this disproportion which actually effects the reduction. Accordingly, the reducing properties studied in this note are a contribution to explain the theoretical foundations of all these titrimetric determinations.

EXPERIMENTAL PART

The following solutions were used:

Ferric sulphate 0.1132N, 0.0566N, 0.1020N and 0.01013N
Potassium thiocyanate 1N and 0.1N
Sulphuric acid 10N
Potassium dichromate 0.0500N and 0.01000N
Mercuric sulphate 1M
Ceric sulphate 0.02N and 0.01N

Influence of the thiocyanate concentration. In every experiment 10 ml of 0.1132N ferric sulphate, 2 ml of sulphuric acid and variable amounts of thiocyanate were taken. The volume is adjusted to 100 ml. The solution was stirred vigorously and the presence of ferric ion was detected in the reduced solution by adding an excess of thiocyanate:

TABLE I

Concentration of KSCN in the solution	Observations
0.25M	Solution decolorised in less than 30 seconds. No precipitate.
0.10M	,, ,, ,,
0.05M	,, ,, ,,
0.03M	Decolorisation takes place more slowly; very small amount of precipitate.
0.02M	Solution decolorised, but with production of a grey (mercury + mercurous thiocyanate) very abundant precipitate.

The experiments carried out in the absence of air yielded the same results.

Influence of ferric ion concentration. A similar technique to the above described was followed, but with thiocyanate at a definite concentration (0.05M) and the ferric concentration variable:

TABLE II

$Fe_2(SO_4)_3$ 0.1132N ml	Observations
10	Rapid reduction with total decolorisation.
15	Rapid reduction with total decolorisation; slight precipitation.
20	Reduction initially very rapid, but subsequently rather slow. Total decolorisation; slight precipitation.
25	Slow reduction. Total decolorisation with production of an abundant grey precipitate.

Dissolution of mercury. A known amount of ferric ion was stirred with a weighed amount of mercury in the presence of 0.1M thiocyanate. When the reduction was complete, the mercury was separated by decantation, washed with water, air dried and weighed again.

TABLE III

Fe^{+3} taken mg	Hg dissolved mg	Hg dissolved (mean value) mg
56.95	103.8	
56.95	104.4	
56.95	104.4	
56.95	104.1	104.1
56.95	103.7	
56.95	104.4	
56.95	104.1	

In these experiments one equivalent of iron correspond to 1.01 equivalents of mercury, in good agreement with the theoretical expectations.

The absence of the air did not affect these results.

Analytical applications

Titration of ferric iron on macroscale

Procedure. The ferric solution containing less than 70 mg of iron in 100 ml was placed in a conical flask. The solution was acidified with 5 ml of concentrated sulphuric acid, and 5 ml of potassium thiocyanate (1*M*) and about 10 ml of mercury was added. The mixture was stirred thoroughly until decolorisation occurred. The reduced solution was separated by decantation, the mercury being washed with dilute sulphuric acid; alternated separation was effected by adding the necessary amount of carbon tetrachloride. 5 ml of mercury sulphate (*M*), 5 ml of phosphoric acid (d = 1.42) and two drops of barium diphenylamino-sulphonate indicator were added and the titration with 0.05*N* dichromate carried out in the usual way. The titration can also be performed with ceric sulphate using ferrous-phenanthroline complex as indicator.

Some of the results obtained are listed in Table IV.

TABLE IV

Fe^{+3} taken mg	$K_2Cr_2O_7$ 0.0500*N* ml	Fe^{+3} found mg	Diff. mg	Diff. %
15.8	5.65	15.8	—	—
31.6	11.35	31.7	+0.1	+0.3
47.4	17.00	47.5	+0.1	+0.2
63.2	22.70	63.4	+0.2	+0.3

Interferences. Hydrochloric acid does not interfere if its concentration is less than 0.1*M*. At greater concentration the masking of the thiocyanate with mercuric ion is disturbed; a greater amount of mercuric sulphate must be added.

Manganous, zinc, titanic, chromic, cadmium, aluminium, nickel, cobalt and bismuth ions do not interfere.

Molybdate, vanadate and cupric ions interfere.

The nitrate ion is reduced and interferes.

Titration of the ferric iron on semimicroscale. The same technique as in the macroscale was followed.

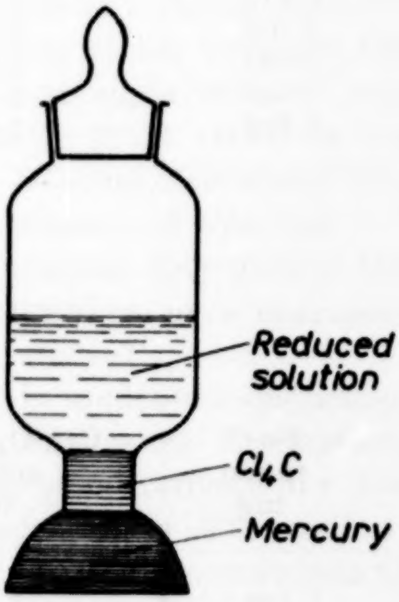

Fig. 1.
Apparatus for micro-reductions with mercury or liquid amalgams.

The separation of the reduced solution, moreover, is simplified by using the apparatus shown in Fig. 1. Its capacity is about 25 ml. When the reduction is finished, it is necesary only to add carbon tetrachloride and the solution is ready for titration.

Procedure. Variable amounts of ferric sulphate solution were added to 1 ml sulphuric acid $10N$ and 1 ml of potassium thiocyanate (total volume 10 ml). Metallic mercury was then added and the solution stirred until decolorisation occurred. 1 ml of $1M$ mercuric sulphate and 1 ml of phosphoric acid (d = 1.42) were added and the solution titrated with dichromate or ceric sulphate in usual way.

Some of the results obtained are listed in the following Tables V, VI and VII.

TABLE V

TITRATION WITH DICHROMATE AND 0.03 ml OF 0.3% BARIUM DIPHENYLAMINOSULPHONATE SOLUTION AS INDICATOR. THE INDICATOR CORRECTION IS 0.03 ml OF DICHROMATE SOLUTION

Fe^{+3} taken mg	$K_2Cr_2O_7$ $0.01N$ correc. ml	Fe^{+3} found mg	Diff. mg	Diff. %
0.566	1.03	0.575	+0.009	+2
0.566	1.04	0.580	+0.014	+3
1.131	2.02	1.128	−0.003	−0.3
1.131	2.03	1.133	+0.002	=0.2
2.262	4.06	2.267	+0.005	+0.2
2.262	4.06	2.267	+0.005	+0.2
2.828	5.00	2.792	−0.036	—1
2.828	5.05	2.820	+0.008	+0.3

TABLE VI

TITRATION WITH CERIC SULPHATE AND POTENTIOMETRIC DETERMINATION OF THE END POINT

Fe^{+3} taken mg	$Ce(SO_4)_2$ $0.02N$ correc. ml	Fe^{+3} found mg	Diff. mg	Diff. %
1.131	1.00	1.117	—0.014	−0.3
1.131	1.02	1.139	+0.008	+0.8
2.262	2.02	2.256	—0.006	−0.3
3.393	3.095	3.378	—0.015	−0.5
3.393	3.04	3.395	+0.002	+0.06

TABLE VII

TITRATION WITH CERIC SULPHATE AND POTENTIOMETRIC DETERMINATION OF THE END POINT

Fe^{+3} taken mg	$Ce(SO_4)_2$ 0.01N correc. ml	Fe^{+3} found mg	Diff. mg	Diff. %
0.566	0.99	0.553	−0.013	−2.6
1.131	2.05	1.145	+0.014	+1.4
1.131	2.01	1.122	−0.009	−0.9
1.697	3.05	1.703	+0.006	+0.3
1.697	3.06	1.709	+0.012	+0.6

IN PRESENCE OF CYANIDE

The enhancement of the reducing power of metallic mercury in the presence of cyanide is produced by the formation of the stable complexes $(CN)_2Hg$ and $[Hg(CN)_4]^{-2}$. The mercury can act as a reductor according to the following equations:

$$Hg + 2\ CN^- \text{ ——— } Hg(CN)_2 + 2\ e$$
$$Hg + 4\ CN^- \text{ ——— } [Hg(CN)_4]^{-2} + 2\ e$$

The theoretical potential of this system in a 0.1 M solution of cyanide and 0.01M of mercuric cyanide complex is about —0.3 v.

In accordance with this potential the above system acts as a strong reductor in an alkaline medium. Since mercuric cyanide is a very stable complex the concentration of the cyanide in the solution is not of great importance, so long as a sufficient amount to form the complex is present; a great excess is not necessary, and there is no possibility of precipitation of some mercurous salt, always dismutate in the presence of great or small amounts of cyanide.

The main inconvenience of this reductor system is the presence of cyanide in the solution, which however, does not matter for many purposes.

The reduction of some oxidising systems has been studied:

Atmospheric oxygen is reduced to hydrogen peroxide. It produces a disturbing effect in the reduction of other substances necessitating its previous elimination.

The reduction of ferricyanide to ferrocyanide proceeds quantitatively in a few seconds. The end of the reduction is marked by the disappearance of the yellow-orange colour of the solution, and can be demonstrated with all the reactions of ferricyanide.

Chromate, vanadate and molybdate ions, which lose their oxidising power in an alkaline medium, are not reduced. Iodate, bromate and chlorate ions are not reduced either, in spite of the theoretical expectations. This can be attributed to a very slow speed of reaction. Manganese dioxide is reduced easily to give a colourless solution containing $[Mn(CN)_4]^{-2}$. Other oxidising anions could not be studied since they oxidise the cyanide.

EXPERIMENTAL PART

Solutions employed:

Potassium ferricyanide 0.0993 and 0.0895*N*
Potassium cyanide *N*
Sulphuric acid 10*N*
Hydrochloric acid conc.
Benzidine acetate sat.
Ceric sulphate 0.0923*N*
Ferrous orthophenanthroline, prepared as usual.

Reduction of atmospheric oxygen. Different 0.1*M* solutions of cyanide were stirred in the presence of the air in a conical flask during one minute. In different portions the presence of hydrogen peroxide and cyanate was tested. The former with titanic sulphate, the latter with alcoholic solution of cobalt acetate. These tests demonstrate the presence of hydrogen peroxide and the absence of cyanate. The following reaction seems consequently most probable:

$$Hg + O_2 + 2\,H_2O + 4\,CN^- \rightarrow [Hg(CN)_4]^{-2} + 2\,H_2O_2 \quad \ldots\ldots \quad (I)$$

and this equation does not seem to take place:

$$H_2O_2 + CN^- \rightarrow CNO^- + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (II)$$

In another experiment 50 ml of 0.1*M* KCN were stirred in the same conditions with mercury in the presence of the air, and the pH mesured with a Beckman pH-meter model G. The pH of the initial solution was 11.0 and after shaking 11.7.

In accordance with these facts, when a solution of cyanide is stirred with mercury and the mercury dissolved determined by weighing, and the hydrogen peroxide present by titration with ceric sulphate[10], the mercury is dissolved in an amount exceeding the hydrogen peroxide found, which also demonstrates the reaction (I). The following equation seems consequently to take place also:

$$2\,Hg + O_2 + 2\,H_2O + 8\,CN^- \rightarrow 2\,[Hg(CN)_4]^{-2} + 4\,OH^- \quad \ldots\ldots \quad (III)$$

Reduction of ferricyanide

Qualitative tests. 10 ml of ferricyanide solution and 5 ml of cyanide solution were diluted to 50 ml and stirred with metallic mercury in a conical flask, in the presence of air. The solution is decolorised. In the reduced solution the ferricyanide, ferrocyanide and hydrogen peroxide were tested. The test for ferricyanide (benzidine acetate in presence of lead acetate) was negative. The test for ferrocyanide (ferric chloride) and the test for hydrogen peroxide (titanic sulphate) were positive. If during these tests the solution is acidulated, the formation of a yellowish colour is noticed, due to the oxidation of the ferrocyanide to ferricyanide by the hydrogen peroxide.

If the same tests are carried out in the absence of air (elimination with pure nitrogen), the formation of hydrogen peroxide does not take place and the reduction of ferricyanide to ferrocyanide seems to be quantitative.

Quantitative studies. 50 ml of solution containing variable amounts of ferricyanide in presence of 0.1*M* potassium cyanide are stirred with 100 g of mercury till decolorisation. The reduced solution is separated by decantation. It is acidulated with 6 ml of 10*N* sulphuric acid and titrated with ceric sulphate. The following results are obtained:

TABLE VIII

$[Fe(CN)_6]^{-3}$ taken mequiv.	$Ce(SO_4)_2$ 0.1*N* correc. ml	Reducing substances present (ferro+H_2O_2) mequiv. mequiv.	H_2O_2 mequiv.
0.496	6.90	0.690	0.194
0.496	7.25	0.725	0.229
0.993	13.00	1.300	0.307
0.993	12.60	1.260	0.267
1.489	16.90	1.690	0.200
1.489	17.20	1.720	0.230

From these results it seems evident that a great and variable amount of hydrogen peroxide is formed.

After some experiments it was found that the hydrogen peroxide could be eliminated by heating the alkaline solution; no interaction between this substance and the ferrocyanide was then observed. It was found that an empirical correction factor (f = 0.1 ml of $Ce(SO_4)_2$) must be applied to obtain correct results.

Procedure. The solution is reduced as above. After decantation, the solution is boiled some minutes, left to stand and cool, acidulated with sulphuric acid and titrated with ceric sulphate.

TABLE IX

$[Fe(CN)_6]^{-3}$ taken mequiv.	$Ce(SO_4)_2$ 0.1*N* ml	$Ce(SO_4)_2$ 0.1*N* correc. ml	$[Fe(CN)_6]^{-3}$ found mequiv.	Dif. mequiv.	Dif. %
0.447	4.61	4.51	0.451	+0.004	+0.8
0.447	4.56	4.46	0.446	—0.001	—0.2
0.447	4.61	4.51	0.451	+0.004	+0.8
0.895	9.04	8.94	0.894	—0.001	—0.1
0.895	8.94	8.84	0.884	—0.011	—1.2
1.342	13.70	13.60	1.360	+0.018	+1.3
1.342	13.60	13.50	1.350	+0.008	+0.6

These results show that in these conditions the reduction of ferricyanide to ferrocyanide is quantitative.

The reduction of other substances

Different solutions of some anions were shaken up together with mercury in the presence of cyanide, following a similar technique to that previously described, chromate, vanadate, molybdate, iodate, bromate and chlorate are not reduced because of their small oxidising power in an alkaline medium.

Analytical applications

In view of the characteristics of the reduction of ferricyanide (very rapid, very clean and easy, selectivity and quantitivity) and in spite of the correction factor to be applied, it seems to us that this reduction could conveniently be applied to the titration of ferricyanide. In this way the ferrocyanide produced is titrated with ceric sulphate.

SUMMARY

The reducing properties of metallic mercury in solutions containing ions forming precipitates or complexes with mercuric or mercurous ions have been studied. The reducing power of mercury in the presence of thiocyanate is greatly enhanced, and it is similar to that in the presence of hydrochloric acid. The effects of the thiocyanate and ferric concentrations have been examined. To reduce a 0.01M solution of ferric ion without forming a precipitate of mercurous thiocyanate, a concentration of thiocyanate of at least 0.05M is required. The action of mercury-thiocyanate system on some oxidising substances has been studied. The most important reaction is the reduction of ferric ions. The method has been applied to the determination of iron on macro and semimicroscale and good results have been obtained.

The reducing power of metallic mercury in the presence of cyanide has also been examined. In general it acts as a strong reducer in alkaline medium. Atmospheric oxygen is reduced partially to water and hydrogen peroxide. Ferricyanide is reduced quantitatively to ferrocyanide. The action of metallic mercury in the presence of cyanide on other oxidising substances has also been examined.

RÉSUMÉ

On a étudié les propriétés réductrices du mercure métallique dans des solutions contenant des ions, formant des précipités ou des complexes avec les ions mercureux ou mercurique. Le pouvoir réducteur du mercure est exalté notablement en présence d'ions thiocyaniques, de la même façon qu'en présence d'acide chlorhydrique.

On a étudié l'influence de la concentration des ions thiocyaniques et ferriques.

Pour réduire une solution 0.01M en ions ferriques, sans formation d'un précipité de thiocyanate mercureux, il est nécessaire d'avoir une concentration 0.05M en thiocyanate. On a examiné l'action du système mercure-thiocyanate sur quelques substances oxydantes. La réaction la plus importante est la réduction des ions ferriques. Cette méthode, appliquée à la détermination du fer à l'échelle macro et semimicro, donne de bons résultats. On a également examiné le pouvoir réducteur du mercure en présence d'ions cyanhydriques. En général, il se comporte comme un réducteur énergique en milieu alcalin. L'oxygène atmosphérique donne de l'eau et de l'eau oxygénée en se réduisant partiellement. L'ion ferricyanhydrique est réduit quantitativement en ion ferrocyanhydrique. D'autre part, on a essayé l'action du mercure métallique, en présence de cyanure, sur d'autres substances oxydantes.

ZUSAMMENFASSUNG

Die reduzierenden Eigenschaften von metallischem Quecksilber sind in Lösungen von Ionen welche mit Mercuri-oder Mercuro-Ionen komplexe Ionen bilden, studiert worden.

Die Reduzierbarkeit von Quecksilber wird in Anwesenheit von Sulfocyanat ziemlich erhöht und sie nähert sich den Werten, die man in Anwesenheit von Salzsäure erhält. Der Einfluss der Konzentration der Sulfocyanat- und Ferri-Ionen wurde untersucht. Um eine 0.01M Ferri-Ionen-Lösung, ohne dass sich ein Niederschlag von Mercurosulfocyanat bildet, zu reduzieren, braucht man eine minimale Konzentration von 0.05M Sulfocyanat. Die Wirkung des Systems Quecksilber-Sulfocyanat auf verschiedene oxydierende Substanzen wurde untersucht. Die wichtigste Reaktion ist die Reduktion der Ferri-Ionen. Diese Methode ist makro- und semimikroanalytisch mit guten Ergebnissen angewandt worden.

Es wurde ebenfalls die Reduzierbarkeit von Quecksilber in Anwesenheit von Cyanid-Ionen untersucht. Im allgemeinem reagiert es im alkalischem Medium wie ein starkes Reduktionsmittel. Atmosphärischer Sauerstoff wird zu Wasserstoffperoxyd und Wasser reduziert. Die Wirkung des metallischen Quecksilbers in Anwesenheit von Cyanid auf andere oxydierenden Substanzen wurde ebenfalls untersucht.

RESUMEN

Se han estudiado las propiedades reductoras del mercurio metálico en soluciones que contienen iones formadores de complejos con los iones mercuriosos o mercúricos.

El poder reductor del mercurio se exalta notablemente en presencia de sulfocianuro, y es semejante al que adquiere en presencia de ácido chlorhídrico. Se ha estudiado el efecto de la concentración de los iones sulfocianuro y férrico. Para reducir una solución 0.01M en ión férrico, sin formación de precipitado de sulfocianuro mercurioso, es necesaria una concentración como mínimo de 0.05M de sulfocianuro. Se ha estudiado la acción del sistema mercurio-sulfocianuro sobre algunas substancias oxidantes. La reacción más importante es la reducción de los iones férricos. El método ha sido aplicado a la determinación del hierro en macro y semimicroescala obteniéndose buenos resultados.

Ha sido también considerado el poder reductor del mercurio en presencia de ión cianuro. En general actúa como un reductor fuerte en medio alcalino. El oxígeno atmosférico se reduce parcialmente a peróxido de hidrógeno y agua. El ión ferricianuro se reduce cuantitativamente a ferrocianuro. Se ha comprobado la acción del mercurio metálico en presencia de cianuro sobre otras substancias oxidantes.

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LE DOSAGE PAR VOIE COMPLEXOMÉTRIQUE DU CALCIUM ET DU MAGNÉSIUM DANS LES MILIEUX TRÈS RICHES EN CHLORURES

(Sel marin brut et saumures)

par

ARTHUR DE SOUSA

Laboratoire de Chimie Physique, Institut Supérieur Technique, Lisbonne (Portugal)

Ayant été amenés à faire un grand nombre de déterminations de calcium et de magnésium dans les saumures et dans le sel marin brut, nous constatons deux inconvénients aux méthodes usuelles: 1° les valeurs erronnées que l'on obtient pour le calcium et le magnésium dans les milieux très riches en chlorures, et 2° la durée de ces analyses.

Les dites déterminations sont importantes pour le commerce du sel. En effet, le calcium et le magnésium, toujours présents dans le sel marin brut et dans les saumures, donnent des propriétés hygroscopiques au produit cristallisé. Il faut donc pouvoir doser rapidement ces deux terres alcalines par un procédé simple où une très grande rigueur n'est pas exigée.

Comme les procédés classiques de la gravimétrie sont surtout longs, nous avons étudié une méthode volumétrique pour la détermination rapide du calcium et du magnésium. Tous les deux peuvent être en effet titrés complexométriquement dans une solution aqueuse de sel ou dans une dilution de saumure, en utilisant comme réactif le sel disodique de l'acide éthylènediaminotétracétique (Complexon III).*

La méthode que nous avons adoptée pour le dosage complexométrique du calcium et du magnésium est très simple et rapide. Il est possible de connaître les teneurs en Ca et Mg d'un échantillon de sel en moins d'une heure, alors que par gravimétrie il faut attendre au moins 24 heures.

De nombreuses analyses gravimétriques du calcium et du magnésium nous ont permis d'établir les limites de concentration de ces deux éléments contenus dans divers échantillons de sel marin brut. Ainsi le calcium peut varier de 0.1 g à 2.5 g par 100 g de sel et le magnésium de 0.2 à 3.0 g.

Grâce aux remarquables travaux de SCHWARZENBACH et de ses collaborateurs[1], sur le titrage du calcium et du magnésium par complexométrie, son emploi a permis la détermination rapide et précise de la dureté calcaire et magnésienne de l'eau.

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* La maison B. Siegfried (Zofingue, Suisse) a bien voulu mettre à notre disposition des échantillons ainsi que des indicateurs pour nos essais.

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Ces auteurs ont trouvé que le purpuréate d'ammonium (Murexide) est un indicateur spécifique du calcium. La coloration bleu violet de l'indicateur en milieu alcalin et en l'absence d'ions Ca^{+2}, vire au rouge violet aussitôt que les ions Ca^{+2} sont présents. En complexant ces derniers au moyen du Complexon III, la coloration bleu violet réapparaît avec une netteté remarquable. Grâce à la spécificité de la Murexide pour le calcium, le magnésium n'a aucune influence sur le dosage du premier. Il convient de se réassurer toutefois, si le sel étudié contient beaucoup de fer et d'aluminium car, en présence de ceux-ci, le dosage du calcium peut être faussé[2]. Nos expériences ont prouvé que le sel marin brut ne contient que des traces de fer et d'aluminium et que le dosage direct de la solution de sel donne de très bons résultats.

Le dosage du magnésium exige un indicateur approprié. SCHWARZENBACH et BIEDERMANN[3] ont trouvé que le colorant diazoïque, connu dans l'industrie sous le nom de noir Eriochrome T, convient tout particulièrement pour le magnésium. Cet indicateur colore une solution aqueuse alcaline ($pH = 10$) en bleu. L'introduction d'ions Mg^{+2} dans cette solution provoque un virage net du bleu au rouge.

Malgré sa grande sensibilité pour les ions Mg^{+2} avec lesquels il forme un complexe, le noir Eriochrome T n'est pas spécifique pour le magnésium, vu qu'il forme aussi un complexe avec le calcium. En d'autres termes, lorsqu'on ajoute l'indicateur à la solution saline, il se forme en premier lieu le complexe de calcium puis celui de magnésium.

Lorsqu'on titre le mélange d'ions Ca^{+2} et Mg^{+2} par le Complexon III, tout le calcium est extrait du complexe indicateur-Ca^{+2} et ce n'est qu'alors que le magnésium se combine avec le réactif. Lorsque tout le magnésium a réagi avec le Complexon III, la solution change de couleur, passant d'un rouge vineux au bleu. En réalité le virage correspond à la quantité totale de réactif nécessaire pour la formation du complexe avec le calcium, puis du complexe magnésien.

Il est aisé de déduire la quantité de magnésium et de calcium en faisant deux titrages successifs, le premier avec la Murexide comme indicateur, ce qui permet de doser le calcium seul, le second avec le noir Eriochrome T qui permet le dosage de la somme $Ca^{+2} + Mg^{+2}$. Ainsi, si N représente la quantité de réactif pour les ions Ca^{+2} et N' celle correspondante à la somme $Ca^{+2} + Mg^{+2}$, la quantité de magnésium se calculera par différence:

$$(N' - N) \times \text{Facteur} = \ldots \text{ g Mg}$$

TECHNIQUE OPÉRATOIRE

Dosage du calcium

Dans un bécher, on dissout 10 g de sel marin brut dans 200 ml d'eau distillée. On y ajoute une solution d'hydroxyde de sodium jusqu'à ce que le pH de la solution soit supérieur à 12. On y verse quelques ml de l'indicateur Murexide jusqu'à l'obtention d'une forte coloration rouge. On titre avec une solution 0.1 *M* de Complexon III (sel disodique de l'acide éthylènediaminotétracétique) jusqu'à ce que l'indicateur vire au bleu violet. Soient *N* ml la quantité nécessaire pour obtenir le virage. La teneur en calcium sera:

$$N \times 0.04008\%$$

Il convient de se servir d'une microburette de 10 ml.

Solution volumétrique

Solution volumétrique. On dissout 37.21 g du sel de Complexon III dans un peu d'eau bidistillée et l'on parfait le volume à 1.000 ml. 1 ml de cette solution correspond à 4.008 mg de calcium.
Indicateur. Solution aqueuse saturée de Murexide. Il convient de ne pas utiliser des solutions plus anciennes que deux semaines.

Dosage du magnésium

On dissout 10 g de sel marin dans 200 ml d'eau distillée contenus dans un bécher. On ajoute environ 1 ml d'indicateur (Noir Eriochrome T) et 10 ml de solution tampon ($NH_4Cl + NH_4OH$) et l'on chauffe entre 40 et 50° C. A ce moment, on titre avec la même solution volumétrique que pour le calcium, jusqu'à ce que la solution vire du rouge vineux au bleu. Il est important que la température de la solution au cours du titrage ne soit pas inférieure à 40° C. Soient *N'* ml de réactif utilisés. La teneur en magnésium du sel marin sera donnée par: $(N'-N) \times 0.02432\%$ Mg, *N* étant le nombre de ml du réactif nécessaire pour titrer le calcium dans l'essai précédent.

Solutions nécessaires

Réactif. Le même que pour le calcium.
Indicateur. 0.4 g de noir Eriochrome T dans 100 ml d'alcool absolu.
Solution tampon. On introduit dans un ballon jaugé de 1000 ml, 54 g de chlorure d'ammonium et 350 ml d'ammoniaque à 25% et l'on parfait avec de l'eau jusqu'au trait de jauge.

CONCLUSIONS

Nous avons procédé à quelques dizaines de déterminations de calcium et de magnésium dans le sel marin brut de diverses provenances et les résultats obtenus par voie volumétrique sont en accord avec ceux obtenus par gravimétrie. L'écart maximum est de 0.5%. La simplicité et la rapidité de la méthode complexométrique est remarquable en face des inconvénients des procédés de la gravimétrie.

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RÉSUMÉ

Une méthode rapide est décrite pour le dosage du calcium et du magnésium dans le sel marin brut et dans les saumures. Les méthodes classiques de la gravimétrie sont très longues et susceptibles d'erreurs lorsqu'elles sont appliquées aux milieux riches en chlorures. Les deux terres alcalines sont dosées par titrage complexométrique, en employant le Complexon III (sel disodique de l'acide éthylènediaminotétracétique) comme réactif et deux indicateurs (la Murexide et le noir Ériochrome T) pour la détermination du calcium et pour celle de la somme des ions Ca^{+2} et Mg^{+2}. La quantité de magnésium est obtenue par différence. Alors que les méthodes classiques de la gravimétrie exigent au moins 24 heures, les deux déterminations peuvent être effectuées dans l'espace d'une heure et avec une rigueur satisfaisante.

SUMMARY

A rapid method is described for the determination of calcium and magnesium in natural sea salts and in brine. The classical gravimetric methods are very lengthy and are susceptible to errors if used in media rich in chlorides. The two alkaline earths are determined by complexometric titration using Complexon III (disodium ethylenediaminetetra-acetate) as reagent and two indicators (Murexide and Eriochrome Black T) for the determination of calcium and for the sum of Ca^{+2} and Mg^{+2} ions. The quantity of magnesium is obtained by difference. While the classical gravimetric methods take at least 24 hours, these two determinations can be effected in 1 hour, giving satisfactory accuracy.

ZUSAMMENFASSUNG

Es wurde eine rasche Methode zur Bestimmung von Calcium und Magnesium im rohen Meersalz und in Salzlaken beschrieben. Die klassischen gravimetrischen Methoden sind sehr langwierig und ergeben unrichtige Werte, wenn sie in mit Chlor angereicherten Lösungen angewendet werden. Die beiden Alkalierden werden durch komplexometrische Titration unter Verwendung von Complexon III (dem Dinatriumsalz der Äthylendiaminotetraessigsäure) als Reagenz und mit Murexid und Eriochromschwarz T als Indikator zur Bestimmung des Calciums und der Summe von Calcium und Magnesium bestimmt. Die Menge des Magnesiums ergibt sich aus der Differenz. Während die klassischen Methoden mindestens 24 Stunden erfordern, können die beiden Bestimmungen in einem Zeitraum von 1 Stunde und mit befriedigender Genauigkeit ausgeführt werden.

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LA DÉTERMINATION INDIRECTE DU TUNGSTÈNE DANS LES MINERAIS PAR VOIE COMPLEXOMÉTRIQUE

par

ARTHUR DE SOUSA

Laboratoire de Chimie Physique, Institut Supérieur Technique, Lisbonne (Portugal)

Les minerais les plus communs du tungstène sont, la wolframite, la scheelite, la ferberite, la hübnerite et l'ocre tungstique.

Les principales impuretés accompagnant ces minerais sont l'étain, l'arsenic, le fer, le plomb, le zinc, le cuivre, le silicium et parfois l'or, l'argent, le titane, l'antimoine, le lithium, le molybdène, le manganèse, l'uranium, le bismuth et le calcium. On y rencontre aussi le phosphore, le béryllium, l'yttrium, le tantale, le nickel, le vanadium et assez fréquemment le bore et le fluor.

Le tungstène apparaît sous forme de sulfure dans la tungsténite, comme oxyde hydraté dans la tungstite, avec du plomb dans le stolzite et la raspite, avec du molybdène dans la powellite et la chillagite, avec du cuivre dans la cuprotungstite et la cuproscheelite.

Le minerai de tungstène le plus fréquemment rencontré au Portugal est la wolframite. On trouve également, mais en quantité plus petite, la scheelite, la ferberite, la hübnerite et la cuproscheelite. D'autres minerais accompagnent la wolframite: la pyrite, la chalcopyrite, la stannite, la galène, l'arsénopyrite, etc., dans leurs formes oxydées. Quelques veines et filons contiennent la muscovite, la tourmaline et la fluorite.

Il est bien connu que la détermination quantitative du tungstène dans ses minerais est une opération assez longue par voie gravimétrique. Même pour des déterminations de routine où une grande rigueur n'est pas exigée, il faut attendre au moins 24 heures pour obtenir le résultat.

Nous avons élaboré une méthode beaucoup plus rapide, et à la fois aussi rigoureuse, pour déterminer indirectement le tungstène, par titrage complexométrique. En effet, le procédé décrit est basé sur la formation du précipité insoluble dans l'eau, de tungstate de calcium. Par décomposition de ce précipité au moyen de l'acide chlorhydrique concentré, on libère le calcium sous forme de sel soluble que l'on titre au moyen du complexon III[1]. Il est aisé de calculer la teneur en WO_3 contenu dans le précipité, en connaissant celle du calcium.

Nous avons vérifié, qu'une solution de tungstate de sodium légèrement alcaline

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(pH = 8) précipite quantitativement sous forme de tungstate de calcium, lorsqu'on y ajoute un excès d'une solution saturée de chlorure de calcium. Le précipité ainsi obtenu pourrait être pesé, mais malheureusement nous avons constaté que, même après 12 heures de séchage, dans l'étuve à 100° C, le poids n'est pas constant. En effet, en poursuivant le séchage pendant 4 heures à 110° C, on observe une différence de poids entre 1 et 1.5%. Le continuant encore durant 2 heures à 120° C, il y a encore une diminution de poids entre 0.1 et 0.3%. Ce qui prouve que le précipité de tungstate de calcium est hydraté contrairement à ce que divers auteurs ont affirmé[2]. Comme nos essais n'ont pas permis de peser directement le précipité de $CaWO_4$ dans un laps de temps suffisamment court, nous avons eu recours au dosage du calcium par titrage complexométrique.

Etant donné que le tungstate de calcium est facilement décomposé en chlorure de calcium et en acide tungstique sous l'action de l'acide chlorhydrique (1:1) chaud, et que le calcium passe quantitativement en solution en laissant le tungstène sous forme de précipité, nous avons titré le premier à l'aide du sel disodique de l'acide éthylènediaminotétracétique, en nous servant de la murexide[3] comme indicateur complexant. Le titrage est rapide et à la fois précis et n'exige pas les nombreuses précautions de la gravimétrie.

Les nombreux travaux sur le dosage du calcium par voie complexométrique suivant la technique de SCHWARZENBACH[4] ont démontré l'efficacité de cette méthode. C'est la raison pour laquelle nous l'avons adoptée. Les résultats que nous avons obtenus sont en bonne concordance avec ceux de la gravimétrie. La méthode décrite et dont la technique sera exposée, sert très bien pour les déterminations de routine du tungstène dans ses minerais. Nos essais de contrôle de la méthode décrite, ont été faits avec des échantillons de wolframite et de scheelite.

TECHNIQUE ADOPTÉE

1 g de minerai finement pulvérisé est fondu dans un creuset de platine avec 7-8 g d'un mélange équimoléculaire de carbonate de potassium anhydre et de carbonate de sodium anhydre. Après la fusion, le bouton est dissous dans de l'eau distillée chaude.

Les résidus, adhérant aux parois du creuset, sont dissous en chauffant le creuset dans un peu d'eau distillée. Les eaux de lavage sont réunies. On chauffe le contenu du bécher et l'on filtre le précipité en le lavant plusieurs fois avec de l'eau chaude.

Le filtrat contient le tungstate de sodium. On ramène le volume à 200 ml environ. Par addition de l'acide chlorhydrique, le pH est amené à une valeur entre 8 et 9. On chauffe à l'ébullition et l'on ajoute 20 à 25 ml d'une solution saturée de chlorure de calcium, également chaude. On laisse bouillir pendant 2-3 minutes puis on laisse refroidir.

La filtration se fait à froid. Le précipité adhérant aux parois du bécher, est lavé à l'eau chaude. Le filtre et le précipité sont également lavés plusieurs fois à l'eau chaude. Le filtrat et les eaux de lavage sont écartés.

Le filtre avec le précipité est introduit dans le bécher où s'est effectuée la précipitation du tungstate de calcium. On y ajoute 20 à 25 ml de HCl (1:1) et l'on chauffe à l'ébullition. Le tungstate de calcium se décompose en acide tungstique et en chlorure de calcium. L'acide tungstique précipite. On filtre en lavant bien le filtre avec de l'eau chaude jusqu'à disparition de l'ion chlorhydrique (essai à la touche avec $AgNO_3$ sur plaque à godets noire).

Le filtrat est amené à volume d'environ 200 ml et l'on ajoute soigneusement de l'ammoniaque jusqu'à ce que le pH de la solution soit entre 12 et 13. On ajoute alors quelques ml d'indicateur (murexide), afin d'obtenir une forte coloration rouge. On titre la solution colorée avec une solution 0.1*M* de complexon III, de manière à ce que la couleur vire au bleu violet.

Un ml de la solution 0.1*M* de complexon III correspond à 4.008 mg de Ca^{+2}. Or, dans le tungstate de calcium, 13.92 parts de calcium correspondent à 63.83 de tungstène ou à 80.53 de WO_3. Un ml de la solution de complexon III correspond donc indirectement à 18.3786 mg de tungstène ou à 23.1867 mg de WO_3.

Solutions nécessaires

a) *Acide chlorhydrique* 1:1

b) *Solution saturée de chlorure de calcium*

c) *Solution* 0.1 *M de complexon III* * (sel disodique de l'acide éthylènediaminotétracétique).

Dissoudre 37.21 g du sel dans de l'eau bidistillée et parfaire le volume de 1000 ml dans un ballon jaugé. Cette solution se conserve pendant assez longtemps, si le flacon est bien bouché et gardé dans un lieu frais.

d) *Indicateur complexant* (*murexide*) * (purpuréate d'ammonium).

On prépare une petite quantité de l'indicateur pour les titrations immédiates, vu qu'il ne se conserve pas plus de 4-5 jours. On prépare 100 ml de solution en dissolvant 0.5 g dans 100 ml d'eau distillée bouillante. Après refroidissement, la solution est prête.

CONCLUSIONS

La détermination du tungstène dans les minerais, par la méthode que nous venons de décrire peut durer 3 à 4 heures. Nous avons pu constater que l'erreur commise (en valeur relative) par rapport à la méthode gravimétrique est inférieure à 0.5% pour les teneurs en WO_3 comprises entre 10 et 25%, et de l'ordre de 0.1% pour les teneurs en WO_3 comprises entre 25 et 70%.

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* Echantillons aimablement mis à notre disposition par la maison B. Siegfried, Zofingue (Suisse).

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Vu sa rapidité et la facilité de la technique, la méthode ci-dessus est à recommander pour les déterminations en série de tungstène dans les minerais. Dans les cas de minerais très pauvres en WO_3, nous recommandons de faire une fusion avec 5 g de substance et de procéder comme décrit (p. ex. le tungstène dans la cassitérite).

RÉSUMÉ

La détermination du tungstène par les méthodes gravimétriques est longue et exige des précautions spéciales. Une méthode simple et rapide est décrite pour la détermination indirecte de tungstène dans les minerais par voie complexométrique.
La séparation du tungstène (sous forme de tungstate de sodium) est obtenu par précipitation au moyen de chlorure de calcium. Le précipité de tungstate de calcium est filtré et décomposé ensuite en chlorure de calcium et acide tungstique (insoluble), en traitant le tungstate de calcium par l'acide chlorhydrique concentré. Le filtrat, rendu alcalin, est titré au moyen d'une solution 0.1*M* de Complexon III. Un ml de cette solution correspond à 23.1867 mg de WO_3. Cette détermination dure 3 à 4 heures.

SUMMARY

The determination of tungsten by gravimetric methods is time-consuming and requires special precautions. A simple and rapid method is described for the indirect determination of tungsten in minerals by means of complexometric titration.
The separation of tungsten (in the form of sodium tungstate) is obtained by precipitation of this soluble salt by means of calcium chloride. The precipitate of calcium tungstate is filtered and decomposed into calcium chloride and tungstic acid (insoluble) by treating with concentrated hydrochloric acid.
The filtrate is made alkaline and serves for the titration with a 0.1*M* solution of Complexon III. One ml of this solution corresponds to 23.1867 mg of WO_3. This determination of tungsten takes 3 to 4 hours.

ZUSAMMENFASSUNG

Die gravimetrische Bestimmung des Wolframs ist zeitraubend und erfordert besondere Vorsicht. Eine einfache und schnelle Methode und indirekten Bestimmung des Wolframs in Erzen mit Hilfe der komplexometrischen Titration wird beschrieben. Die Abtrennung des Wolframs (als Natriumwolframat) wird durch Fällung dieser löslichen Salze durch den Zusatz von Kalziumchlorid erreicht. Der Niederschlag von Kalziumwolframat wird filtriert und nachher durch Behandlung mit konzentrierter Salzsäure in Kalziumchlorid und unlösliche Wolframsäure zersetzt. Das Filtrat wird alkalisch gemacht und dient zur Titration mit einer 0.1*M* Komplexon III Lösung. Jede ml dieser Lösung entspricht 23.1867 mg WO_3. Diese Bestimmung des Wolframs dauert 3 bis 4 Stunden.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURES OF SULFONAMIDES VII

by

P. L. DE REEDER

Zwijndrecht (Netherlands)

*IV. The bromometric titration of the sulfonamide-molecule**

This determination is based on the fact that the benzene nucleus and, in some compounds, the heterocyclic nucleus of the sulfonamide-molecule is readily substituted by electrophilic reagents, like bromine and iodine, according to
$H_2NC_6H_4SO_2NH\text{-}R + 2Br_2 \rightarrow H_2NC_6H_2Br_2SO_2NH\text{-}R + 2HBr$ or
$H_2NC_6H_4SO_2NH\text{-}R + 3Br_2 \rightarrow H_2NC_6H_2Br_2SO_2NH\text{-}RBr + 3HBr$.
Substitution by the former has found very extensive use as a means of assaying simple sulfonamides, while the use of the latter in this respect has been restricted to a few cases.

The performance of the bromometric titration meets with some difficulties. This is reflected in the literature, which includes a large number of instructions, advices and remarks concerning the method. These various instructions can be divided into two groups, each presenting a solution for one of the two difficulties that are met with in the performance of the determination.

A. An excess of bromine (in the form of potassium bromide and potassium bromate) is added to a solution of the substance in hydrochloric acid. After a certain bromination-time (varying from 0 to 60 minutes) the excess bromine is titrated back.

Advantage over method B: rather sharp end-point in the iodometric back-titration (though, according to CONWAY[83], not a very stable one).

Disadvantage: many compounds tend to be oxidated and over- or underbrominated. To get reproducible results, one has to adhere to strictly defined conditions like time of bromination, excess of bromine and temperature.

B. An acid solution of the sulfonamide, containing potassium bromide and a suitable indicator, is titrated with potassium bromate solution till the dye is destroyed by one drop of excess bromate.

Advantage over method A: almost no danger of overbromination or oxidation.

Disadvantage: rather unsharp end-point.

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* See schedule in *Anal. Chim. Acta*, 9 (1953) 142.

The end-point can be determined potentiometrically SRINIVASAN[84]). We prefer the use of a dye as indicator, however, to elaborate a method that can be used in small laboratories not possessing a potentiometer (*cf.* our first paper).

Of course, many modifications of the two methods have been suggested to avoid the difficulties indicated. Some of these modifications will be discussed below.

A very important feature of method A is the mutual divergence of the bromination-times of the various compounds. Since the bromination does not take place in sharply distinguished steps and, therefore, does not come to an end after the formation of (say) the dibromo-derivative, it is important to stop the reaction after the formation of the desired derivative (mostly the dibromo-derivative). The proper bromination-times vary considerably from compound to compound, as may be seen from Table XIII, in which a number of bromination-times from the literature are listed (time in minutes). Even for one compound differences are apparent; they may partially be attributed to differences in temperature, solvent, etc.

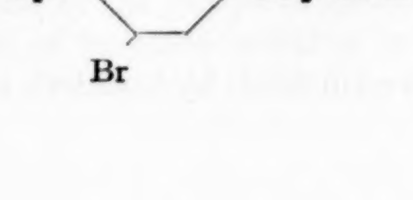
TABLE XIII

Compound	Reference								
	85	86	87	83	81	88	5	89	90
Irgafen		20							
Irgamid		60							
Soluseptazine									
Sulfacetamide		2	5						
Sulfadiazine		5		1½	5-10	0			
Sulfamerazine		5		1½					
Sulfamezathine		2							
Sulfanilamide	5		5	1½		0	5		
Sulfaguanidine		2		1½				45	
Succinylsulfathiazole				1½					
Sulfapyridine		⅙	⅙				5		
Sulfathiazole	5	5	120	1½					5

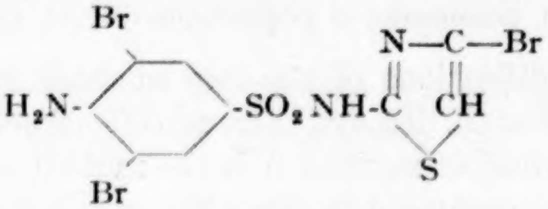
From the figures given method A appears not to be very suitable for application to mixtures. In this respect method B seems to be more appropriate.

WOJAHN[91] has found a high acidity of the solution to be titrated of great advantage. In contrast to the usual acidity of 5% hydrochloric acid he employs a concentration of 25%. This presents the following important advantages:

1. The rate of bromination is increased to such an extent that well-defined reaction products are formed without a certain bromination-time.
2. All compounds investigated yield a dibromo-derivative with the structure



Sulfathiazole is an exception, since it forms a tribromode-rivative:



The following compounds were investigated by WOJAHN: sulfanilamide, sulfapyridine, sulfacetamide, septazine, sulfathiazole and some other ones of less importance.

Figures from Table XIII indicate that the rates of formation of these various derivatives are different at other acidities (the acidities commonly used in method A being mostly much lower).

3. Since in WOJAHN's method free bromine is only present in the solution during a short time (*cf.* the performance of the titration below), there is no risk for side-reactions due to oxidation.

Another method that seemed to be of much value to us is described by CONWAY[83]. He applies a high concentration of acetic acid and a uniform bromination-time of two minutes. The addition of a large amount of acetic acid prevents the precipitation of the reaction-products. On the other hand, iodine and sodium thiosulfate cannot be used for the back-titration of the excess bromine, since sometimes insoluble coloured addition-products between the iodine and the dissolved bromine compounds are formed, giving false results (*cf.* WOJAHN[91]).

The second peculiarity of this method is the fact that the bromination-time of 2 minutes holds for all compounds investigated (*cf.* Table XIII). The method can, therefore, be applied to mixtures. There remains, of course, the drawback of the presence of free bromine that can cause oxidation.

The direct bromometric titration, mentioned above, which seems very attractive by way of its simplicity and rapidity, has not been investigated very profoundly. WOJAHN[91] determined the end-point by the discoloration of previously added indigocarmine, or by the persistence of the yellow colour of free bromine. The end-point can be made more easily visible by diluting the solution with the same amount of glacial acetic acid, which prevents the precipitation of the reaction products. The paper by DOLEŽAL AND SIMON[98] may also be mentioned here.

We now come to the discussion of our own investigations. We used and compared the following methods:

1. Method of WOJAHN[91] (determination using excess bromine).
2. Method of CONWAY[83] (excess bromine).
3. Method of WOJAHN[91] (direct titration).
4. Method of CONWAY[83] (direct titration).

Performances:

1. The compound was dissolved in dilute hydrochloric acid (3%) and concentrated

hydrochloric acid (30-35%) added until the solution contained 25% HCl. After this 3 g of potassium bromide was added and then 0.1 *N* potassium bromate solution *slowly* from a buret until a yellow colour persisted.

1 g of potassium iodide was then *immediately* added and the iodine titrated with thiosulfate.

2. The compounds were dissolved in 10 ml dilute sodium hydroxyde (2%), with the exception of soluseptazine (dissolved in water), irgafen and irgamid (dilute hydrochloric acid with heating), sulfaguanidine (glacial acetic acid). The solution was placed in a glass-stoppered vessel and to it were added successively: 1.5 g of solid potassium bromide, a small excess of a 0.2 *N* solution of potassium bromate, 80 ml of glacial acetic acid and finally 5 ml of concentrated hydrochloric acid. The flask was immediately stoppered, shaken for 30 seconds and set aside for 1.5 minute. The excess bromine was then back-titrated with a 0.1 *N* solution of arsenic trioxide. End-point: the disappearance of the yellow colour of the bromine.

3. The same performance as method 1, but now the solution was titrated with the potassium bromate solution until the disappearance of the colour of 4-5 drops of a methyl red solution (0.1% in alcohol), previously added.

In some instances an equal volume of glacial acetic acid was also added to the solution to be titrated (see below).

4. The same performance as method 2; however, to the solution of the compound were now added: the potassium bromide, the glacial acetic acid, the hydrochloric acid and 5 drops of a methyl red solution. Next, the solution was titrated with the 0.2 *N* solution of potassium bromate until the disappearance of the red colour.

Before discussing the results obtained with the various methods we will first give some remarks concerning our practical experiences.

1. In the titration after WOJAHN (excess bromine) a precipitation of the bromo-substitution products is often yielded. This has no influence upon the results, however.

The rate of reaction between the free bromine and the sulfonamide proved to be high at the beginning of the reaction and to slow down at the end. The solution then remains yellow after the addition of one drop of bromate. Therefore, if the bromate is added too quickly, free bromine exists in the solution for too long a time, giving rise to interfering side reactions. Therefore, when reaching the point of equivalence it is highly advisable (in this as well as in the other three methods) to add the potassium bromate *very slowly* drop by drop.

2. In the titration after CONWAY (excess bromine) no precipitation occurs, except in the case of irgafen, when the bromo-substitution products proved to be insoluble even in glacial acetic acid.

The excess of free bromine must be taken as low as practically possible, to avoid unnecessary losses due to the escape of gaseous bromine from the solution while shaking. The excess of bromate solution is best taken as large as one millilitre.

Since the quantity of hydrochloric acid present is much smaller than in Wojahn's method, the reaction rate is much lower, which can clearly be seen while adding the bromate solution.

3. In the direct titration after Wojahn the great drawback occurs that the precipitate of the reaction-products absorbs part of the indicator (methyl red). This part is decolorized only when an excess of bromine is present. Thus the quantity of bromine reacted is estimated too high.

It is very troublesome to determine the correct end-point in the turbid solution therefore. In this respect we prefer the addition of glacial acetic acid resulting in a clear titration-liquid (*cf.* above).

4. In the direct titration after Conway the reaction rate is rather small (*cf.* 2). Therefore the bromine formed is not immediately used up in the substitution-reaction, and has the opportunity to oxidize the indicator. In our experience this premature oxidation cannot be completely prevented. It can, however, be reduced as far as possible by means of the following two measures.

a. At the end the liquid is titrated *very slowly*. The colour then also fades, but does not disappear before the end-point is reached. Besides, while fading the colour remains distinctly *red*; at the end-point it turns colourless or very faintly yellow. This turnover is not abrupt, since the oxidation of the indicator also takes a few seconds.

b. The indicator is not added until the end-point is nearly reached (*e.g.* when half a millilitre of bromate has yet to be added). This requires a previous trial-titration, of course.

TABLE XIV

Compound	Excess bromine Wojahn %	Excess bromine Conway %	Direct titration Wojahn %	Direct titration Conway %	
Irgafen	93.4	91.8	90.6	95.1	Calcd. as dibromo-derivative
Irgamid	81.7	65.8	82.2	59.5	Calcd. as tetrabromo-derivative
Sulfacetamide	99		99		Figures from the literature
Sulfadiazine	99.9	100.4	99.6	100.0	Cacld. as tribromo-derivative
Sulfamerazine	99.6	100.3	99.7	99.8	Calcd. as tribromo-derivative
Sulfamezathine	100.2	104.2	100.3	101.3	Calcd. as dibromo-derivative
Sulfamethylthiazole	104.6	104.0	103.1	109.9	Calcd. as tribromo-derivative
Sulfathiazole	98.3	98.6	98.0	97.7	
Sulfapyridine	100.1	100.9	99.9	100.8	
Sulfanilamide	99.2	99.7	99.2	99.5	No precip. in Wojahn's method
Sulfaguanidine	99.8	99.7	99.6	99.8	
Septazine	99.9	106.7	99.6	101.3	

We now come to the discussion of our results. They are summarized in Table XIV, to which the following remarks must be made.

Irgafen* is difficult to brominate. WOJAHN[92] has found that a dibromo-derivative is yielded in strong acid solution after a bromination-time of 20 minutes; our low values are thus to be attributed to this low reaction-rate.

Irgamid* contains a double bond. This compound also has a low reaction-rate, even in strong acid solution (WOJAHN[92]).

Soluseptazine gave very indistinct results. No indication has been obtained of the formation of a well-defined reaction product, as can be seen from the following evaluation of our titration-figures (Table XV):

TABLE XV

Calculation assuming that one molecule of soluseptazine consumes:	Excess bromine		Direct titration	
	WOJAHN %	CONWAY %	WOJAHN %	CONWAY %
8 atoms of bromine	73.2	31.2	64.3	37.7
6 ,, ,, ,,	97.4	40.4	85.6	50.3
4 ,, ,, ,,	144.9	60.0	127.6	74.8
3 ,, ,, ,,	195.1	80.6	171.5	100.5

We cannot confirm, therefore, the results of CHAPMAN AND PIERCE[76], who established the formation of a tetrabromo-derivative.

LAPIÈRE AND LENAERS[24] were not able to determine sulfamerazine and sulfamezathine owing to oxidation of the methyl groups. We, however, noted hardly any interference of this side-reaction with sulfamerazine, and only a small one with sulfamezathine. With sulfamethylthiazole oxidation obviously occurs to a greater extend. It is not yet quite clear why the direct titration results in more oxidation than excess bromine during 1.5 minute.

Surveying the results, we can conclude the following.

1. The method that gives the best results as well as the sharpest end-point is the determination using an excess bromine after WOJAHN. Since this excess of bromine is immediately used up after the addition of potassium iodide it hardly can cause oxidation. There is no extra bromination-time. Though the addition of the bromate solution from the buret must happen slowly, this is more convenient than the direct titration with an unsharp end-point (methyl red).

2. The methods described can only be applied to the following sulfonamides: sulfacetamide, sulfamezathine, sulfapyridine, sulfanilamide, sulfaguanidine and septazine (calcd. as dibromo-derivatives); sulfadiazine, sulfamerazine, sulfamethylthiazole and sulfathiazole (calcd. as tribromo-derivatives).

The other compounds give more or less deviating results.

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* Dissolved in a few ml of ammonia (3%) previous to the addition of the acid.

Succinylsulfathiazole and elkosin could not be studied, since the quantity of material available was not sufficient for an extensive investigation.

Finally a number of mixtures was investigated. They only contained compounds each of which gave good results for itself. The results are summarized in Table XVI. As can be seen from the figures given there the bromometric assay of the sulfonamides in a mixture can very well be performed, provided that they *all* belong to the above-mentioned group. Fortunately this is true of all compounds that are of great therapeutic value to-day.

TABLE XVI

Compound	Quantity in g	Excess bromine Wojahn %	Excess bromine Conway %	Direct titration Wojahn %	Direct titration Conway %
Sulfadiazine	0.12013				
Sulfamerazine	0.12009	99,6	100,6	99.5	98.7
Sulfamezathine	0.12020	99.9	101.3	99.8	99.3
Sulfadiazine	0.12013	99.4	99.8	99.5	99.7
Sulfamerazine	0.12009	99.7	100.0	99.3	99.7
Sulfadiazine	0.12013	101.5	104.5	99.9	101.0
Sulfamezathine	0.12020	100.8	104.1	100.1	101.2
Sulfadiazine	0.12013				
Sulfamerazine	0.12009	98.7	99.3	98.9	98.6
Sulfathiazole	0.11891	99.0	99.0	99.1	98.7
Sulfathiazole	0.11891	98.9	101.5	98.6	99.3
Sulfamezathine	0.12020	99.0	102.2	98.8	99.6
Sulfapyridine	0.12050	99.8	100.3	99.7	99.9
Sulfadiazine	0.12013	100.1	100.7	99.8	100.1

Approximately 6 g of each of the compounds mentioned was dissolved in as small a quantity of 2% NaOH as possible, and then filled up to 500 ml. The different mixtures were prepared by combining every time 10 ml of these solutions.

V. *The nitrite-titration of the free aromatic amino group*

In many Pharmacopoeias this titration is used in the assay of tablets, ointments, etc. which contain a sulfonamide as the active compound. Many investigators, however, look upon this determination as a means of orientation only: Gauthier[81], Conway[83], Lapière *et al.*[24]. This is caused by the difficulty of establishing the correct end-point. As a rule, 0.2-0.4 g of the compound is dissolved in an excess 3-4% hydrochloric acid and titrated with 0.1 *N* sodium nitrite. The end-point is attained when one drop of the solution spotted on potassium iodine-starch paper yields *immediately* a blue colour, which lasts 40-60 seconds. The judging of this colour now offers some difficulty since a colour already occurs before an excess nitrite is present*.

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*This prevents the addition of potassium iodide-starch to the solution as a normal internal indicator.

This one is blue with a distinct reddish tint, and is not immediately yielded, but only after a few seconds. Excess nitrous acid causes immediately a dark blue, sometimes nearly black, colour, which, however, fades quickly. Moreover, at the end of the titration, the reaction-rate is rather low, so after each addition of nitrite the solution is only spotted on the reagent-paper after one minute.

Some investigators tested the suitability of internal indicators to detect the end-point: FROST[93], CONROY[94], ÅGREN[95], but none was found to be satisfactory.

The end-point can also be determined potentiometrically: LA ROCCA AND WATERS[96], MCNAUGHTON *et al.*[97]; this method seems to give better results than the use of indicators.

In our own investigations we found the old way of spotting a drop of the titration-liquid on potassium iodide-starch paper rather accurate, in contrast to the many objections mentioned above. It is true that at the end the titration must be performed quite slowly, and that some experience in judging the colours is necessary; but, when analyzing pure sulfonamides, we always obtained very good results (99-100% recovery). We think there is no need to communicate this part of our work in great detail here; some general remarks may suffice to introduce the use of the method to the analysis of mixtures.

Since the reaction-rate is direct proportional to the concentration of hydrochloric acid (ÅGREN[95]), we dissolved nearly 0.5 g of the compound in 100 ml 8% hydrochloric acid and titrated this solution at room temperature with 0.1 N sodium nitrite. No cooling with ice is necessary: this would only decrease the rate of the diazotization reaction (FROST[93], ÅGREN[95]). For the colours obtained with iodide-starch paper see above.

Since the determination depends on the reaction between sodium nitrite and the free aromatic amino group, only sulfonamides which contain this group can be determined. This is thus not the case with succinylsulfathiazole, septazine and soluseptazine. Methods have been worked out to determine the latter using the nitrite titration after previous hydrolysis (CHAPMAN AND PIERCE[76]). This has not been further studied by us.

The nitrite titration of mixtures of sulfonamides has been reported twice: LAPIÈRE *et al.*[24], who assayed a mixture of sulfamerazine, sulfadiazine and sulfathiazole (recovery 100.3%) and WOJAHN[91], who analyzed a mixture of sulfanilamide and marfanil (the latter not reacting with nitrite) (recovery 100.3%).

In Table XVII we give a survey of our determinations of (self-made) mixtures. The performance was the same as described above. Mixtures were prepared from the quantities indicated by mixing well in a weighing-bottle. From the mixtures so obtained the quantity necessary for an analysis was weighed off.

The figures indicate that the nitrite titration is very well suited to the quantitative analysis of mixtures of sulfonamides. It thus provides one more datum to evaluate the unknown composition of the mixture from the corresponding set of equations, as has been outlined in the previous paper.

TABLE XVII

Compound	Quantity in g	Found %
Sulfadiazine	0.7243	99.8
Sulfamerazine	0.6097	99.7
Sulfamezathine	0.6544	
Sulfanilamide	0.8170	98.9
Sulfapyridine	0.6983	99.3
Sulfathiazole	0.5274	99.5
Sulfamezathine	0.5980	98.9
Sulfamerazine	0.6071	99.6
Sulfathiazole	0.7279	99.7
Sulfapyridine	0.7308	99.5

SUMMARY

The application of the bromometric titration and of the nitrite titration on mixtures of sulfonamides is discussed. Four different performances of the bromometric titration were investigated, one giving good results with mixtures. The nitrite titration, using an external indicator, proved also to be well suited.

RÉSUMÉ

L'application de la titration bromométrique et de la titration au nitrite, aux mélanges de sulfamidés est discutée. Quatre méthodes différentes de titration bromométrique ont été examinées, l'une donne de bons résultats avec des mélanges. La titration au nitrite, en présence d'un indicateur externe convient également.

ZUSAMMENFASSUNG

Die Anwendung der bromatometrischen Titration und der Nitrit-Titration auf Mischungen von Sulfonamiden wird besprochen. Vier verschiedene Ausführungen der bromatometrischen Titration wurden untersucht; eine gab gute Ergebnisse mit Gemengen. Die Nitrit-Titration, in welcher ein äusserliches Indikator verwendet wurde, zeigte sich auch sehr geeignet.

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THE RAPID SEPARATION AND ESTIMATION OF TITANIUM BY MEANS OF ETHYLENEDIAMINETETRA-ACETIC ACID

by

W. F. PICKERING

Newcastle College, N.S.W. University of Technology, Tighes Hill (Australia)

Low percentages of titanium are very satisfactorily estimated by the colorimetric method which is based on the yellow colour developed when hydrogen peroxide is added to an acid solution of the titanium salt[1].

However, there are several common elements which will interfere in this estimation and if present, the titanium must either be given a preliminary separation or a corresponding amount of interferant added to the comparison standard. Among the interferants may be listed iron, nickel and chromium which interfere because of the colour of their solutions; vanadium, molybdenum and cerium which form coloured compounds with hydrogen peroxide; and fluorine (even in minute amount), large amounts of alkali salts or phosphates all of which bleach the colour.

Many separation procedures have been suggested for the isolation of the titanium from one or more of the interfering elements and among these may be mentioned the removal of iron, cobalt, nickel and zinc by the passage of hydrogen sulphide through an ammoniacal tartrate solution; the removal of iron by extraction with ether; the separation of titanium, iron, vanadium, tungsten from aluminium, chromium, manganese, nickel and phosphorus by precipitation with cupferron; fusion with sodium carbonate or precipitation with sodium hydroxide which will separate iron and titanium from molybdenum, vanadium, phosphorus, aluminium and hexavalent chromium; and the use of electrolysis with a mercury cathode which will separate titanium, vanadium, aluminium and others from iron, chromium, nickel, molybdenum and other electropositive metals[2].

Recently, PŘIBIL AND SCHEIDER[3] determined titanium gravimetrically by precipitating it as the hydroxide whilst using Complexon III (di-Na salt of ethylenediaminetetra-acetic acid) to complex interferants. Manganese and chromium co-precipitated but iron, mercury, copper, lead, bismuth, cadmium and nickel remained in solution, 0.5 to 5 hours being required for complete separation of the titanium.

The alternative to separation procedures, namely the addition of a similar

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interferant to the standard solution, is not always satisfactory since it demands a previous knowledge of the amount of interferant present but it has the advantage of speed over the standard separation procedures.

The new technique discussed below may be described as a modification of the method of PŘIBIL AND SCHEIDER but in this case the titanium estimation may be completed fifteen to twenty minutes after solution of the sample.

EXPERIMENTAL

The major part of this investigation was concentrated on the separation of small amounts of titanium from large amounts of iron but equally satisfactory results were obtained in the presence of nickel, vanadium, molybdenum, manganese and chromium if the latter was given a preliminary oxidation to the hexavalent state. The method used in this study and suggested for general application is as follows:

To an acid solution (HCl or H_2SO_4) containing the titanium and interfering elements add an excess of the di-Na-salt of ethylenediaminetetra-acetic acid to complex the cations. In the presence of 1 g of NH_4Cl, make the solution ammoniacal, iron if present, forming a red complex which will serve as indicator.

The solution should be thoroughly cooled at this stage and have a volume of about 50 ml. Add 10 to 20 ml (depending on amount of Ti present) of 10% magnesium sulphate solution and agitate briskly for several minutes.

Filter off the precipitate formed and wash with dilute ammoniacal solution. This precipitate contains all the titanium and some magnesium salt.

Dissolve the precipitate in warm 5% sulphuric acid and test for complete solution of the titanium by washing the filter paper with hydrogen peroxide, any remaining yellow being carefully washed through into the filtrate with further acid.

Dilute the coloured filtrate (containing at least 5 ml of 3% H_2O_2) to a standard volume and compare with standard titanium solutions.

Notes on the method

a) The weight of complexon required to give an excess will vary with the form of complexon used. With Commercial Trilon B, the weight required will be approximately seven times the weight of metal cations present but if the anhydrous di-Na-salt or the free acid is used the ratio can be reduced to six.

b) The amount of magnesium sulphate solution added should be sufficient to give an appreciable precipitate which will carry down all of the titanium but very large amounts may break up the iron complex and give a contaminated precipitate. In the cold 10 ml of a 10% solution were found to be adequate, but when the Ti content was greater than 5 mg the amount was increased slightly.

c) The precipitate obtained should be white in colour and any creamy tinge indicates co-precipitation of iron or other cations, and if the colour is excessive it is advisable to add a little phosphoric acid to the solution before comparison. The creamy precipitate generally indicates insufficient complexon in the original solution.

d) The precipitate may be filtered through filter paper or a sintered glass crucible but the author found the use of a small Buchner funnel and flask to be the most rapid and convenient means of filtration.

e) The sulphuric acid used for solution of the precipitate is most conveniently administered from a wash bottle. It is advisable to give the precipitation flask a rinse with acid to dissolve the small amount of precipitate which adheres to the walls of the vessel. Neglect in testing the filter paper for remaining traces of Ti can result in appreciable losses.

Mixtures of titanium and other elements were prepared from standard solutions of these elements and treated as above. The coloured solutions were compared in a Coleman Universal Spectrophotometer using a wavelength of 425 $m\mu$ (maximum absorbance of the Peroxide colour) and the results obtained are tabulated below.

TABLE I

Wt Fe present	Wt Ti taken	Wt Ti recovered	Wt Fe present	Wt Ti taken	Wt Ti recovered
0.05 g	2.0 mg	2.10 mg	0.10 g	10.0 mg	9.90 mg
0.10 g	0.10 mg	0.10 mg	0.10 g	10.0 mg	10.00 mg
0.10 g	0.25 mg	0.23 mg	0.25 g	2.0 mg	2.00 mg
0.10 g	0.50 mg	0.53 mg	0.25 g	10.0 mg	10.00 mg
0.10 g	0.75 mg	0.73 mg	0.50 g	1.0 mg	0.98 mg
0.10 g	1.00 mg	1.00 mg	0.50 g	2.0 mg	2.00 mg
0.10 g	2.0 mg	2.03 mg	0.50 g	5.0 mg	5.00 mg
0.10 g	3.0 mg	3.00 mg	0.50 g	7.5 mg	7.50 mg
0.10 g	4.0 mg	4.05 mg	0.50 g	10.0 mg	10.10 mg
0.10 g	5.0 mg	4.90 mg	1.0 g	2.0 mg	2.00 mg

TABLE II

Wt of interferant present	Wt Ti taken	Wt Ti recovered
5 mg V	5.00 mg	4.98 mg
40 mg V	2.00 mg	1.98 mg
0.1 g Cr^{+6}, 0.1 g Mn^{+7}	5.00 mg	5.00 mg
0.2 g Cr^{+6}, 0.2 g Ni, 0.01 g Mo, 0.01 g V, 0.03 g Mn, 0.25 g Fe	5.00 mg	5.04 mg

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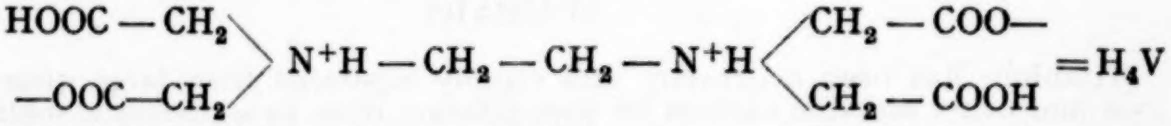
In the absence of suitable titaniferous iron ore samples, two synthetic samples were prepared by intimately mixing rutile-ilmenite beach sand concentrates with haematite ore. 0.2 g portions of these samples were fused with potassium pyrosulphate, leached with sulphuric acid and the titanium content estimated colorimetrically after a separation from interfering elements by the above method and also after a mercury cathode separation. The comparative results obtained are given in Table III.

TABLE III

Sample No.	% Ti - Complexon method	% Ti-Hg Cathode separation
1	4.80	4.94
	4.87	4.90
	4.87	4.88
2	0.73	0.70
	0.73	0.75
	0.70	0.73

DISCUSSION

Ethylenediaminetetra-acetic acid behaves virtually as a strong dibasic acid, and it is usually represented[4] as a betaine structure.



$$\begin{array}{l} \mathrm{HOOC-CH_2} \\ \mathrm{—OOC—CH_2} \end{array} > \mathrm{N^+H-CH_2-CH_2-N^+H} < \begin{array}{l} \mathrm{CH_2-COO—} \\ \mathrm{CH_2-COOH} \end{array} = \mathrm{H_4V}$$

This dihydrogen versenate ion reacts with many metallic ions on a one to one molar basis to form complex ions:

$$e.g.\ M^{+2} + (H_2V)^{-2} \rightarrow (MV)^{-2} + 2H^+$$

According to BLUMER AND KOLTHOFF[5] titanium complexes of the form TiV^- and TiV are formed at pH 2.5-1, and a tentative dissociation constant calculated from polarographic data was given as $K_{TiV} = 2 \cdot 10^{-18}$. However, with higher pH values the electrode processes become irreversible and the presence of complexes containing oxygen and numerous nuclei was assumed.

In ammoniacal solution the instability is sufficient to allow the titanium to precipitate on standing, which fact has been used in its separation[3,6]. The addition of magnesium sulphate to the cold ammoniacal solution produced a crystalline precipitate which contained all of the titanium present. The crystalline precipitate may be composed of magnesium versenate (generally accepted as being soluble) which acts as a carrier for a precipitate of hydrated titanium oxide or alternatively the precipitate obtained in this assay may be an insoluble titanium complex

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containing magnesium in the nuclei. This magnesium does not interfere with the colorimetric estimation of the titanium.

However, tervalent chromium is also precipitated by this procedure and if present should be given a preliminary oxidation to chromate before addition of the Complexon. In this condition, no contamination of the precipitate was noted, the chromate passing through into the filtrate.

All other common interfering cations in the colorimetric estimation of titanium will remain in solution as stable complexes and the separation is virtually complete. With Ti contents ranging from 0.1 to 10 mg and in the presence of from 10 to 1000 times its weight of iron, the mean recovery of titanium was 100 ± 1.5% of that present.

CONCLUSIONS

By using the salts of ethylenediaminetetra-acetic acid to complex interfering cations, small amounts of titanium may be rapidly estimated by precipitation in ammoniacal solution followed by colorimetric comparison.

The order of accuracy of the recovery is high and because of the simplicity of the method should be applicable to any colorimetric titanium estimations where interfering metallic cations are known to be present. The application to titaniferous iron ores has been shown in this paper and work is at present being carried out on the analysis of titanium in high alloy steels.

SUMMARY

Titanium has been accurately and rapidly separated from large quantities of iron and other metallic cations by precipitation from an ammoniacal solution containing excess di-sodium salt of ethylenediaminetetra-acetic acid, the presence of magnesium ions being used to accelerate precipitation. The titanium may then be determined colorimetrically using the yellow colour developed by hydrogen peroxide.

RÉSUMÉ

Le titane peut être séparé rapidement et avec précision de grandes quantités de fer et d'autres cations métalliques, par précipitation au moyen du sel de sodium de l'acide éthylènediaminotétracétique, en solution ammoniaquale. La présence d'ions magnésium accélère la précipitation. Le titane est ensuite dosé colorimétriquement en utilisant la coloration jaune qu'il donne avec le peroxyde d'hydrogène.

ZUSAMMENFASSUNG

Titan wurde genau und schnell von grossen Menge Eisen und anderen Metallkationen durch Ausfällung aus einer einen Überschuss des Dinatriumsalzes der Äthylendiamintetraessigsäure enthaltenden ammoniakalischen Lösung abgetrennt, wobei die Gegenwart von Magnesium zur Beschleunigung der Ausfällung benützt wurde. Titan kann dann kolorimetrisch unter Benutzung der mit H_2O_2 entstehenden gelben Farbe bestimmt werden.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE

II. THE DETERMINATION OF FLUORIDE IN WATERS AND SEWAGE EFFLUENT USING THE ALUMINIUM-HAEMATOXYLIN COMPLEX

by

(Miss) J. S. BEVERIDGE, G. J. HUNTER AND B. J. MACNULTY

Chemical Inspectorate, Ministry of Supply, Kidbrooke, London, S.E.3 (England)

INTRODUCTION

The recently developed method of determining fluoride with the aluminium-haematoxylin reagent[1] appeared to be ideally suited for the direct determination of fluoride in waters. The method has been applied to sea-water, river-water, sewage effluent and drinking-water, and it has been shown that for a fluoride content greater than 0.1 p.p.m., in the absence of interfering ions, direct determination (*i.e.* without prior separation of fluoride by distillation as hydrofluosilicic acid) is satisfactory. In this paper each type of material is considered under a separate heading with appropriate tables and a general discussion of the results is given at the end.

The early investigations were directed to the determination of fluoride in sea-water since little work on this subject had been carried out and the methods available appeared to be unsatisfactory, mainly owing to the very low concentrations encountered.

THE DETERMINATION OF FLUORIDE IN SEA-WATER

The greater part of early work on this problem is of little value and recent literature contains only two references: the work of THOMPSON[2] whose figures refer to the east coast and continental shelf of North America, and that of MIYAKE whose 'Chemical Studies in the Western Pacific Ocean' makes only scant reference to fluoride.

THOMPSON used a modification of DE BOER'S[4] method in which the destruction of the zirconium-alizarin lake by fluoride is the basis for colorimetric determination of that element. This method suffered from the disadvantage that both chloride and sulphate interfered, and that although the effect could be eliminated by addition of equal amounts to the standards with which the sea-water was compared, the method was so sensitive to variation in chlorinity of sea-water that accurate determination of this was required on every sample before reliable fluoride determination could be made. We have checked THOMPSON's method but find it more difficult to carry out than he suggests; the accuracy he claims cannot be obtained readily.

MIYAKE used the method of THOMPSON and found results varying between 1.28 and 1.36 p.p.m. The mean figure for the fluoride content of normal sea-water obtained by THOMPSON was 1.4 p.p.m. (1400 mg/cubic metre) and by MIYAKE 1.3 p.p.m. (1300 mg/cubic metre).

Experimental

Experience in using the reagent had shown that large quantities of foreign ions might alter the colour intensity, without otherwise affecting its usefulness in determining fluoride. It was considered advisable, therefore, in the direct application to use a blank of artificial sea-water. The following solution based on that given by HARVEY[5] was found to be satisfactory and was used in all experiments.

ARTIFICIAL SEA-WATER

Sodium chloride	23.477 g
Magnesium chloride	4.981 g
Strontium chloride	0.024 g
Boric acid	0.026 g
Sodium sulphate	3.917 g
Calcium chloride	1.102 g
Potassium chloride	0.664 g
Potassium bromide	0.096 g
Sodium bicarbonate	0.192 g

Dissolve the above in order in 800 ml of water and make up to one litre. To show that sea-water would cause no serious interference with the method, calibration graphs were constructed (as previously described[1]) using artificial sea-water in place of 20 ml of the distilled water, this being the amount of sea-water sample to be used in later experiments. Results (Tables I and II) showed that direct application of the method without prior separation of fluoride was feasible. Direct applications to sea-water using artificial sea-water as a blank were then carried out, results being shown in Table III.

The results in Table III were obtained against a blank of artificial sea-water and therefore the figures must be corrected for any fluoride in the materials used to make this.

Fluoride determination was carried out on the artificial sea-water, after concentration by evaporation and separation as hydrofluosilicic acid by distillation; the results were 0.22, 0.19, 0.14, 0.14, 0.17, 0.17 p.p.m. giving a mean of 0.17 p.p.m. which must be added to the results in Table III to give the true value of the fluoride content of the sea-water, which is therefore 1.33 p.p.m.

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TABLE I

THE EFFECT OF FLUORIDE ON THE REAGENT IN THE PRESENCE OF ARTIFICIAL SEA-WATER

Fluoride μg/25 ml	△ Absorbancy × 10³						
5	—	59	—	—	—	—	—
10	—	109	—	105	102	116	114
15	—	—	—	—	—	—	159
20	235	—	209	211	225	207	—
25	—	299	267	—	—	—	261
30	362	—	320	—	—	—	—
35	—	—	—	364	399	—	—
40	446	—	—	—	—	410	—
45	—	513	—	—	—	—	—

TABLE II

COMPARISON OF EFFECT OF FLUORIDE ON REAGENT IN DISTILLED WATER AND ARTIFICIAL SEA-WATER

Fluoride	△ Absorbancy × 10³	
μg/25 ml	Distilled water	Artificial sea-water
10	105	107
20	220	213
30	335	324
40	463	422
50	595	522

TABLE III

APPARENT FLUORIDE CONTENT OF SEA-WATER IN P.P.M.

Fluoride added	Fluoride recovered	Apparent fluoride content of sea-water
—	1.15	1.15
—	1.15	1.15
—	1.19	1.19
—	1.15	1.15
—	1.13	1.13
—	1.14	1.14
—	1.17	1.17
—	1.19	1.19
—	1.21	1.21
—	1.19	1.19
—	1.15	1.15
0.5	1.65	1.15
0.5	1.65	1.15
0.75	1.88	1.13
1.0	2.15	1.15

The method was finally checked by concentrating 100 ml samples of sea-water to 10 ml in the distillation apparatus (experiments showed that this treatment did not lead to loss of fluoride), separating the fluoride by distillation, and determining the fluoride as previously described[1]. Results are shown in Table IV.

TABLE IV

FLUORIDE CONTENT OF SEA-WATER IN P.P.M. DETERMINED BY SEPARATION BY DISTILLATION, AND TREATMENT WITH ALUMINIUM-HAEMATOXYLIN REAGENT

Fluoride added	Fluoride found	Fluoride content of sample
—	1.23	1.23
0.5	1.78	1.28
0.5	1.91	1.41
0.5	1.88	1.38
—	1.27	1.27
—	1.39	1.39
—	1.39	1.39
—	1.30	1.30
—	1.30	1.30

In view of the apparent slight decrease in sensitivity when calibration graphs were prepared in the presence of artificial sea-water instead of distilled water a check on the pH values obtained at various stages of the method was made and compared with similar values obtained in the absence of sea-water. The results showed that in the presence of sea-water the final pH was 4.78, which is a little different from that used in previous work[1] but is still within the range at which satisfactory results can be obtained and no advantage would be gained by altering it.

DETERMINATION OF FLUORIDE IN SEWAGE EFFLUENT

Certain samples of sewage effluent were available and the opportunity was taken of testing the method on these. Since the samples all contained a certain amount of sludge it was considered advisable to separate the fluoride by distillation before carrying out the determination. 50 ml samples were used in the first instance and to some of these fluoride was added. Results are shown in Table V.

These results, whilst quite satisfactory, showed the fluoride content of the samples to be very low. Accordingly for further experiments 400 ml of sample were taken, the pH noted and water evaporated off in the distillation apparatus until only 50 ml remained (the solutions were approximately neutral and therefore loss of fluoride was reduced to a minimum). The fluoride was then separated and determined as before. Results are shown in Table VI. An attempt to determine the fluoride directly on 25 ml of the samples gave somewhat low results (see last column of Table VI).

TABLE V

Fluoride added µg	Fluoride recovered µg	Mean apparent fluoride* content of sample in p.p.m.
0	16	
0	18	
0	10	0.3
0	15	
0	16	
0	16	
50	62	
50	64	1.2
50	60	
100	102	
100	106	2.1
100	107	

* Apparent fluoride = True fluoride + added fluoride.

TABLE VI

Sample No.	pH of sample	Fluoride content in p.p.m.	Fluoride content p.p.m. determined directly on the sample
1	7.64	0.25	0.15
2	7.19	0.23	0.13
3	7.07	0.21	0.14
4	7.00	0.27	0.16
5	6.90	0.28	0.17

DETERMINATION IN RIVER AND POTABLE WATERS

The method was been applied to five samples of river-water and three samples of drinking-water, both directly and after separation of the fluoride as hydrofluosilicic acid. Where prior separation of fluoride was used the sample was evaporated to small bulk under conditions previously used satisfactorily for concentrating sea-water. Some river-water contained appreciable quantities of solid material, this was included in the sample where fluoride was separated by distillation but, where fluoride was determined directly, the sludge was allowed to settle out before an aliquot of the sample was removed.

Experimental

Determination of fluoride after separation by distillation

After thoroughly shaking the sample a suitable volume (determined by the fluoride content found in a trial experiment) was placed in the distillation flask. The pH was checked as being close to a value of seven, and the solution evaporated to 50 ml. 50 ml of concentrated sulphuric acid (18*M*) were added carefully and the fluoride separated by distillation in the normal manner and determined with the aluminium-haematoxylin reagent. Results are shown in Tables VII and VIII.

Direct determination of fluoride

A 25 ml sample was taken after the solid matter, where present, had been allowed to settle out. The fluoride was determined directly with the aluminium-haematoxylin reagent. Results are shown in Tables VII and VIII.

TABLE VII

FLUORIDE CONTENT OF, AND RECOVERY FROM, RIVER-WATER

Source of sample	Vol. of original sample taken (ml) for separation of fluoride by distillation	Fluoride added μg	Fluoride found after separation by distillation μg	Fluoride content of sample p.p.m.	Fluoride found directly p.p.m.
River Thames at London					
High Tide	100	0	67	0.67	
		80	140		
Half Tide	100	0	31	0.31	0.36
		80	112		
River Medway	100	0	110	1.09	1.21
	100	0	108		
		80	184		
River Mersey Before entry of Manchester Ship Canal	400	0	46	0.12	0.12
	400	80	136		
After entry of Manchester Ship Canal	400	0	108	0.27	0.24
	400	80	190		
River Clyde	400	0	53	0.13	0.16
	400	80	138		
River Severn	400	0	30	0.08	0.11
	400	80	104		
River Dee	400	0	24	0.06	

TABLE VIII

FLUORIDE CONTENT, AND RECOVERY FROM, POTABLE WATER

Source of sample	Vol. of original sample taken in ml for separation of fluoride by distillation	Fluoride added µg	Fluoride found after distillation µg	Fluoride content of sample p.p.m.	Fluoride found directly p.p.m.
Lancashire	400	0	10	0.025	—
		80	85		
London	400	0	53	0.13	0.07
		80	129		
Surrey	400	0	24	0.06	0.03
		80	96		

DISCUSSION

The results obtained, using the aluminium-haematoxylin reagent to determine fluoride in the various waters, have shown that, in the absence of interfering ions, the determination can be carried out directly. The levels at which extraneous ions would be likely to interfere can be found from the extensive tables of interferences given in Part I[1]. Fluoride contents below 0.1 p.p.m. require concentration by careful evaporation before direct determination, otherwise the accuracy is low.

Direct determination in sea-water is satisfactory but it is advisable to calibrate in artificial sea-water, since there is a slight difference between calibrations in this and distilled water. Any fluoride in the artificial sea-water must be known and it is determined after separation as hydrofluosilicic acid in the usual manner. The mean fluoride content of sea-water from the Atlantic off the British Isles is found to be 1.33 p.p.m.

The samples of sewage effluent contained only a small amount of fluoride and as expected some sludge. Direct determination gave a fluoride content lower by about 0.1 p.p.m. than that obtained after concentration of the solution and separation of the fluoride by distillation.

Provided the fluoride is above 0.1 p.p.m. the determination in river and potable waters can be carried out directly without any great loss of accuracy, though this may not hold in rivers when the sample is taken close to the out flow of industrial effluents.

In the case of the River Thames there is considerably more fluoride present at high tide than at half tide; this is probably due to extra fluoride brought in by the sea-water.

ACKNOWLEDGEMENT

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SUMMARY

The application of the aluminium-haematoxylin reagent to the determination of fluoride in sea-water, river- and potable waters, and sewage effluent is described. It has been shown that down to a level of about 0.1 p.p.m. the fluoride can be determined directly (*i.e.* without prior separation by distillation); there is some loss in accuracy for amounts of the order of 0.2-0.5 p.p.m. With sea-water, calibrations should be carried out in a blank of artificial sea-water. The fluoride contents of a number of British rivers etc., are given.

RÉSUMÉ

Les auteurs proposent d'utiliser le complexe aluminium-hématoxyline comme réactif pour le dosage des fluorures dans l'eau de mer, l'eau de rivière, les eaux potables et les eaux usées. Pour des teneurs en F^- d'environ 0.1 p.p.m., la méthode peut être appliquée directement (sans distillation préalable). La précision est moins bonne pour des quantités de l'ordre de 0.2 à 0.5 p.p.m. Dans le cas d'une eau de mer, un étalonnage doit être effectué à blanc, avec une eau salée artificiellement. Les teneurs en F^- d'un certain nombre de rivières anglaises sont données.

ZUSAMMENFASSUNG

Es wird die Anwendung des Aluminium-Hämatoxylin Reagenzes zur Bestimmung von Fluorid in Seewasser, Flusswasser, Trinkwasser und Abwasser beschrieben. Es wurde gezeigt, dass bis zu einer Konzentration von ungefähr 0.1 Millionstel das Fluorid direkt (d.h. ohne vorhergehende Abtrennung durch Destillation) bestimmt werden kann; es tritt ein geringer Verlust an Genauigkeit bei Mengen der Grössenordnung von 0.2-0.5 Millionstel auf. Eichungen mit Vergleichsproben von künstlichem Seewasser sollten bei der Bestimmung von Seewasser durchgeführt werden. Der Fluoridgehalt einer Reihe britischer Flüsse usw. wird gegeben.

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2,6-BIS(2-PYRIDYL)PYRIDINE AND ALKYL DERIVATIVES. THEIR PROPERTIES IN THE FORMATION OF FERROUS AND COBALTOUS COLORED COMPLEX CATIONS

by

DONALD H. WILKINS AND G. FREDERICK SMITH

Department of Chemistry, University of Illinois, Urbana (U.S.A.)

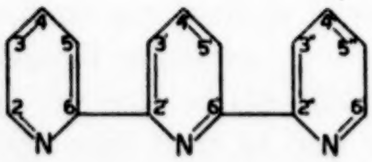
INTRODUCTION

The study of 2,6-bis-(2-pyridyl)-pyridine (originally designated as 2,2′,2″-terpyridine) in the spectrophotometric determination of Fe(II) has been made by MOSS AND MELLOM[1] and as the colored Co(II) complex[2] by the same authors. This organic ligand may be prepared as described by MORGAN AND BURSTALL[12], and is now commercially available.

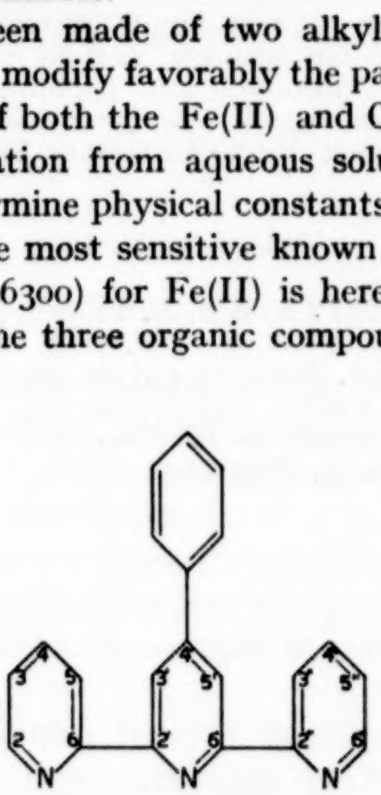
The present study has been made of two alkyl substituted derivatives of 2,6-bis(2-pyridyl)-pyridine to modify favorably the parent compound in order to increase the color intensity of both the Fe(II) and Co(II) colored complex cations, provide for their isolation from aqueous solution by use of immiscible alcohol solvents, and to determine physical constants important in their spectrophotometric adaptations. The most sensitive known chelating compound (molecular extinction coefficient 26300) for Fe(II) is herein described.

The structural formulae. The three organic compounds being compared are as follows:

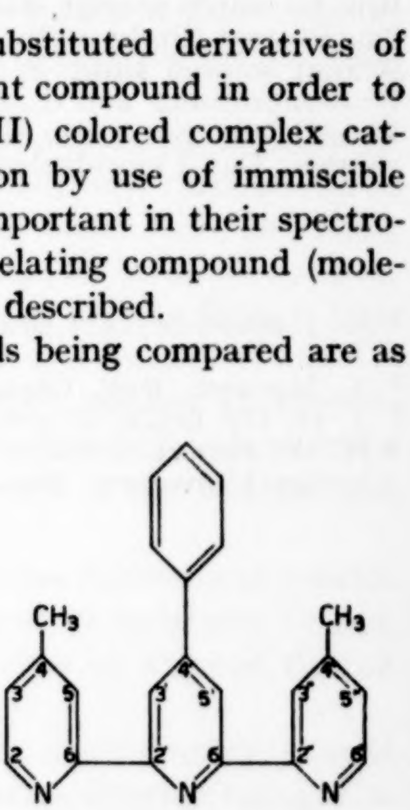
I



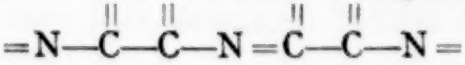
II



III



The functional group from each compound (I, II and III) with the trivial names, "terpyridine," "terosine" and "terosole", respectively, is



$$=N-\overset{\|}{C}-\overset{\|}{C}-N=\overset{\|}{C}-\overset{\|}{C}-N=$$

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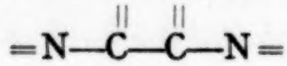
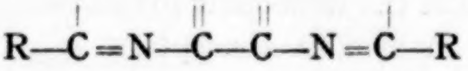
and is given the trivial name of the "terroine" functional group as suggested by the well-established "ferroine" functional group,



$$=N-\overset{\|}{C}-\overset{\|}{C}-N=$$

of the dipyridines and 1,10-phenanthrolines and the "cuproine" functional group,



$$R-\overset{|}{C}=N-\overset{\|}{C}-\overset{\|}{C}-N=\overset{|}{C}-R$$

of the diquinolines. The "terroine" reaction is analogous to the "ferroine" reaction in chelation to form Fe(II) cations, and to the "cuproine" reaction forming Cu(I) complex cations.

Previous studies. The systematic study of a series of methyl-, chloro-, bromo- and nitro-1,10-phenanthrolines had been made by Smith and Richter[3]. A study of symmetrically substituted methyl dipyridines has been made by Cagle and Smith[4]. A survey study of 25 polysubstituted methyl alkyl 1,10-phenanthrolines was made by Brandt and Smith[5] including determination of the wavelength of the ferroine and ferriin cations and the redox potentials in 0.1 and 1.0 normal acid solution of the ferriin-ferroine half cell reactions in redox indicator studies. A study of 28 mono-, di-, tri-, and tetra-methyl substituted 1,10-phenanthrolines, and their cuproine reaction Cu(I) chelated cations was reported by McCurdy and Smith[6]. Special applications of the various ferroine and cuproine reactions in spectrophotometric determinations of Fe(II) and Cu(I) employing the best selections from the extensive list of possibilities, have been described by Cagle and Smith[7] and by Smith and Brandt[8] in dichromate redox reactions at low acidity and by Smith and McCurdy[9] and by Smith, McCurdy and Diehl[10] in the spectrophotometric determination of copper. The "cuproine reaction" was first given this trivial name by Hoste in his studies of biquinolines[11]. The cuproine ligand "neo-cuproine", 2,9-dimethyl-1,10-phenanthroline, was described by Smith and McCurdy[9]. Other related studies in the field are omitted in the interests of brevity.

Preparation of materials. The best procedure in the prepatarion of I, (terpyridine), is in the pyrolytic reaction of dehydrogenation of pyridine-ferric chloride mixtures employed for the simultaneous synthesis of dipyridine as described by Morgan and Burstall including terpyridine and cited by Smith[12].

The preparation of Compound II (terosine) was described by Reiner[13]. Benzaldehyde, 2-acetylpyridine, and aqueous NH_3 were reacted in a sealed glass tube in an autoclave for 180 minutes at 250°. The tarry reaction residue was digested with ethanol and filtered. The tan residue was crystallized from nitromethane. Yield 17%, m.p. 208°. This is a modified Tschitschibabin reaction[13].

The synthesis of compound III (terosole) was provided by Francis H. Case of Temple University. A description of this synthesis is to be published, together with related materials, at a later date.

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Spectrophotometric characteristics of terpyridine, terosine and terosole, as bis-complex, Fe(II) cations.

These ligands provide the basis for the terroine reaction, analogous to the ferroine reaction of 1,10-phenanthroline, except that bis-, instead of tris-complex cations result. A reproduction of the spectrophotometric absorption curves of terosole Fe(II) chelates from which the molecular extinction coefficient E was calculated, and the wavelength of maximum absorption λ_{max} was determined, are shown in Fig. 1. The values calculated for these absorption curves with increasing concentration of iron were found to be 26448, 25562, 26435, 26180, 26555, giving an average of 26300 with a probable accuracy of ±100. The dilution of the *n*-hexyl alcohol extract of the colored complex was to 25 ml and a 1 cm quartz cell was used for the operation. The iron taken is shown below Fig. 1. The comparable determination of the E and λ_{max}, values of the Fe(II) chelates of terpyridine and terosine are given in Table I. These values were determined without extraction (since the terpyridine complex does not extract and the terosine complex is extracted only by multiple operations).

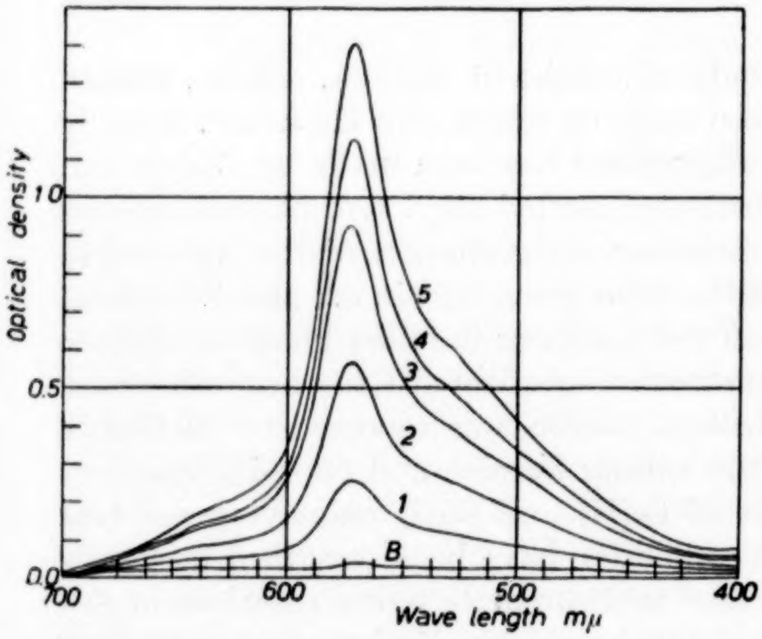


Fig. 1. No. 1 to No. 5 respectively 0.01161, 0.04701, 0.05947 and 0.07189 mg Fe

Terpyridine, terosine and terosole. Spectrophotometric properties as bis-complex, Co(II) cations

Of ligands I, II and III, studies by MOSS AND MELLON[2] of the terpyridine Co(II) complex has been previously reported. The value of E therein determined was 1160 and the complex found non-extractable. Terosine and terosole likewise form colored Co(II) complexes and, as with the Fe(II) chelates, the latter two ligands have increased E values and the colored complex is extractable, particularly favorable in the case of terosole. This fact greatly increases the value of the reagent by magnifying the color intensity to a profitable extent. The spectrophotometric absorption curves for these three Co(II) ligands are shown in Fig. 2 and the data for E and λ_{max} are tabulated in Table I.

Substituted 2,6-bis-(2-pyridyl)-pyridines and resulting modification in properties

The substitution of methyl groups for the 3,3′-positioned hydrogens of 2,2′-dipyridine very materially lowers the tendency towards Fe(II) chelation (from $E = 8650$ to $E = 1770$). The substitution of alkyl groups in one or more of the 3,3′, 3″-positioned hydrogens of terpyridines would be expected to have the same effect. It has been previously shown that 3,3′-dicarboxylic acid-2,2′-dipyridine does not form a Fe(II) complex. This indicates that a planar configuration due to free rotation of the pyridine rings about the common 2,2′-pivot bond has been distorted. It can also be shown that the same effect is obtained when chelation with Cu(I) is attempted. Here a bis- and not a tris-complex is also prevented from forming for the same reason given for Fe(II) chelation.

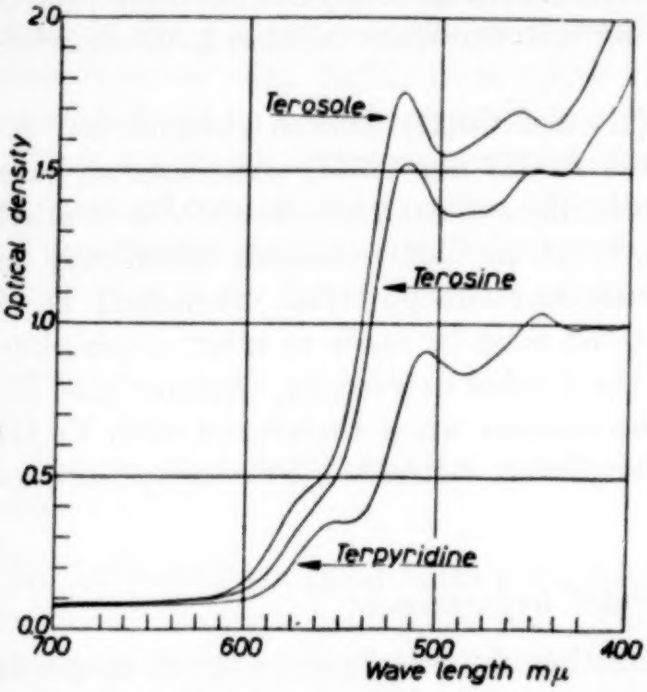


Fig. 2. Spectrophotometric curve of terpyridine, terosine and terosole cobalt (II) complexes

Therefore, when alkyl substitutions such as CH_3 or C_6H_5 are being contemplated in proposed modification of the terpyridine molecule, the 3,3′, 3″-substitutions would be predicted to promote objectionable effects. Their substitution in the 5,5″-positions would be predicted to give some effective changes in properties. As would be predicted from further comparison with 2,2′-dipyridine

TABLE I

SPECTROPHOTOMETRIC CONSTANTS OF THE TERROINE FE(II) AND CO(II) REACTION COMPLEX CATIONS OF TERPYRIDINE, TEROSINE AND TEROSOLE

Compound	Wavelength maximum absorption, max.			Molecular extinction coefficient, E		
	Fe(II) cation	Co(II) cation		Fe(II) cation	Co(II) cation	
Terpyridine	552	444	506	12500	1420 = 444 mμ	1240 = 506 mμ
Terosine	569	452	417	22000	2630 = 452 mμ	2690 = 517 mμ
Terosole	575	457	519	26300	2440 = 457 mμ	2514 = 519 mμ

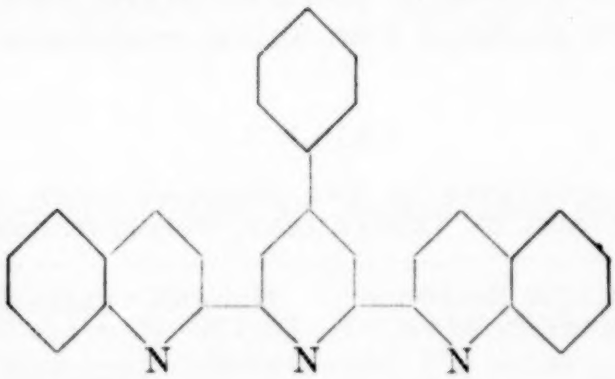
methyl substituted derivatives[4], the best positions for substitutions in the terpyridine molecule are the 4,4′, 4″-hydrogen atoms.

Ligands I, II and III with their increasing molecular weight become progressively less soluble in water as would be predicted. This difficulty can be counteracted by the conversion of the water insoluble form to the water soluble hydrochloride of the organic base.

Ligands I, II and III form both Fe(II) and Co(II) colored chelates but no colored Cu(I) complex cation. Neither the Fe(II) nor Co(II) complexes of I are extractable from solution employing immiscible solvent alcohols such as *iso*amyl or *n*-hexyl alcohol. Compound II forms a Fe(II) or Co(II) complex which may be extracted using these immiscible solvents, but the partition coefficient is so unfavorable that three successive extractions must be made to effect a complete separation from the aqueous phase into the alcohol extractant. Organic base III with its more extensive alkyl group substitutions when complexed with Fe(II) and Co(II) is readily and practically completely extracted by *n*-hexyl alcohol in one operation.

Steric hindrance effects for 6,6″-substituted terpyridine

It is a well-known fact that the substitution of methyl groups for hydrogen in the 6,6′-positions of 2,2′-dipyridine and in the 2,9-positions of 1,10-phenanthroline inhibits the ferroine reaction (chelation with Fe(II)), but not the cuproine reaction (chelation with Cu(I)). Likewise substitutions in the same positions of an additional carbon ring (such as in the case of 2,2′-diquinoline as compared to 2,2′-dipyridine) the Fe(II) chelation is prevented. In the similar case of the compound of structural formula* 2,6-bis-(2-quinolyl)-4-phenylpyridine does not chelate with either Fe(II) or Co(II). It would therefore appear certain that methyl or phenyl substitutions for the 6,6″-positioned hydrogens of terpyridine would inhibit the terroine reaction of chelation also.



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* This compound was prepared by Professor FRANCIS H. CASE of Temple University, Philadelphia, and submitted for test examination.

Proposed substituted terpyridine bases

Newly synthesized terpyridines should provide hydrogen substitutions by alkyl groups such as CH_3 and C_6H_6 preferably in the 4,4′, 4″-positions. The phenyl group in the 4 position of the central pyridine ring raises the *E* value in the terroine reaction with Fe(II) from 12500 to 22000. The same reaction employing compound III as ligand increases the value of *E* from 22400 to 26300. If the 4,4′, 4″-tri-phenyl substituted terpyridine (proposed trivial name "terosite") can be prepared, one might predict a terroine Fe(II) reaction to give an *E* value for this ferrous chelate of approximately 30000. Similar trends may be expected in the case of the Co(II) terroine reaction.

Terosole as a precipitant for perchlorate anions in the presence of nitrate and sulfate

In the isolation of terpyridine from the products of the MORGAN AND BURSTALL synthesis[12] the high boiling fraction (greater than 315° C) of the oil bases, containing probably a number of unidentified oils, the perchloric acid additive of terpyridine was found to be insoluble in water. By this conversion the terpyridine was readily isolated from the contaminating unidentified oils. By dissolving the terpyridine perchlorate in boiling water, in which it is appreciably soluble, followed by filtration on paper, the contaminating oils could be readily removed. By cooling the filtrate pure terpyridine perchlorate was recovered and converted back to free terpyridine.

For these reasons it was predicted that compounds II and III would likewise form insoluble perchlorate addition compounds, insoluble to probably a greater extent because of the increased molecular weight.

Terosole was found to form an extremely insoluble perchlorate. An aqueous solution of Fe(II) at pH 3-4 containing perchloric acid in small amounts was shaken in a separating funnel with a solution of terosole in *n*-hexyl alcohol. Instead of the terroine reaction resulting with the accompanying immediate production of the characteristic color, the terosole formed a flocculent white precipitate which passed into the supernatant *n*-hexyl alcohol extraction layer.

The insolubility of the terosole perchlorate in *n*-hexyl alcohol is of such value that the formation of the terosole Fe(II) chelate, which would be predicted to have a high value instability constant, was not able to compete with the terosole base for the perchlorate anion.

The presence of HCl, HNO_3 or H_2SO_4 did not result in the formation of insoluble terosole addition products under the same conditions. Thus terosole gives promise as a companion reagent to nitron for the precipitation of the perchlorate ion without simultaneous precipitation of the nitrate ion.

Stability of the ferrous complex cation of terosole

The loss in color intensity of the Fe(II) complex cation of terosole was found to be less than one percent after a period of 130 hours and extraction (extracted procedure employing *n*-hexyl alcohol as immiscible solvent with dilution from added ethanol), with storage under ordinary laboratory conditions. The complex cation at pH 2 to 5 in aqueous solution is not decolorized at the boiling temperature. This is in sharp distinction from the loss in color of the Fe(II) chelate of 1,10-phenanthroline which is decolorized under similar conditons at 50-60° C. The terosole Fe(II) cation is formed over the pH range of 2 to 5 and once formed is stable over the pH range of 2 to 10. At pH = 1 the color fades out in approximately 5 minutes. Once the complex is formed the extraction process is applicable over the pH range 1 to 10.

Stability of the Co(II) complex cation of terosole

The Co(II) complex cation of terosole color is not as stable as the Fe(II) chelate under ordinary conditions of exposure to light and contact with air. The extracted complex shows less than 2% diminution in color intensity in 24 hours. This fact enables one to construct an absorbancy-concentration graph without difficulty, but serves as a handicap if color comparisons are to be made using Nessler tube techniques. The color intensity of the Co(II) complex of terosole being only one-tenth as great as that of the Fe(II) chelate, the use of Nessler tube color evaluation is not an attractive procedure under ordinary conditions. The Co(II) complex cation of terosole in aqueous solution has an E value a little greater than the E value for the MnO_4^- anion (2515 compared to 2340), but the ability to extract the complex terosole Co(II) adds very materially to the sensitivity.

Cations and anions which constitute interferences

For these studies the most sensitive terroine reactant, terosole, was selected for study of interferences. The terosole Fe(II) complex cation resulting from the presence of 0.022 milligrams of Fe was formed in the presence of 100 milligrams of a series of anions and cations. To the solution containing the known portion of iron and foreign ions in a 50 ml separatory funnel, there was added a solution of hydroxylamine hydrochloride in excess, and a pH of 2 to 4 provided by the addition of a sodium acetate solution. An excess of terosole in *n*-hexyl alcohol solution was then added and the contents of the separatory funnel shaken for two minutes after the final addition of *n*-hexyl alcohol to total 10 ml. The color complex was allowed to separate from the aqueous portion during 5 minutes standing and the aqueous layer withdrawn. The colored alcohol layer in the separatory funnel was then transferred to a 25 ml calibrated flask. The separatory funnel was rinsed with ethanol and the washings added to the volumetric flask and diluted to the mark with ethanol and thoroughly mixed. The optical density was then determined at 575 mμ. Greater than 2% deviation in optical density was considered to constitute an interference. The following ions were chosen to be typical samples and were found to give no interference: Mn^{+2}, Al^{+3}, Cr^{+3}, and the alkali and alkaline metals, PO_4^{-3}, $P_2O_7^{-4}$, $C_2O_4^{-2}$, Cl^-, NO_3^-, Ac^-, SO_4^{-2}. The following materials constitute interferences: Cu^+, Ni^{+2}, Co^{+2}, F^- and ClO_4^-. The interference of cobalt may be eliminated by adding ethylene diamine to complex cobalt. The interference of the perchlorate anion has been previously explained as due to terosole perchlorate insolubility.

The terroine reaction is favored in the pH range of 2 to 5. Once formed the complex is stable over the pH range of 2 to 10. The reagent precipitates in solutions of pH 5 or greater. The color extracts quantitatively employing *n*-hexyl alcohol over the pH range 1 to 10. At pH 1 the color of the complex Fe(II) cation is dissipated in 5 minutes.

Procedure employed in the preparation of pure cobalt sulfate to be used as reference standard

For the determination of the *E* value of the cobalt complex cations herein described, pure cobalt sulfate was required. The procedure employed in its preparation was as follows:

40 g of cobaltic hexamine chloride, $Co(NH_3)_6Cl_3$, was heated to 200°C. The blue residue was treated with 100 ml of concentrated nitric acid, evaporated to dryness and heated in an electric muffle at 300°C for a period of 6 hours. The oxide thus obtained was dissolved by the addition of 100 ml of 72 per cent. perchloric acid and 100 ml of water. An excess of concentrated sulfuric acid was added and the cobalt perchlorate converted to cobalt sulfate by evaporation followed by baking at 500°C during 5 hours. The resulting product was stored under anhydrous conditions and served as primary standard in the preparation of cobalt solutions.

The determination of iron in presence of cobalt

From an examination of the spectrophotometric curves of Figs. 2 and 3 it will be seen that at wavelength of maximum absorption for the Fe(II) complex cations of terpyridine, terosine and terosole, the extent to which the corresponding Co(II) complex cation absorbs is appreciable. The same situation is met with at λ_{max} for the Co(II) complex, that of the Fe(II) complex absorption being appreciable.

If iron is to be determined in the presence of cobalt, means must be provided to complex the cobalt(II) cation so as to mask it out of possible chelation with the organic ligand in the formation of the Fe(II) colored complex. This was found possible through the use of ethylenediamine. Terosine was found to be adequate as reagent.

Known amounts of iron and of cobalt were transferred to 25 ml graduated flasks and adjusted to pH 4 to 5 by use of an acetate buffer after the addition of excess hydroxylamine hydrochloride. Ethylenediamine (0.3-0.5 ml) was then added and a small excess of the solution of 0.01 molar terosine hydrochloride. The solution thus made was diluted to volume in the flask and the colored solutions then measured using a Cary Model M spectrophotometer. The data thus obtained are given in Table II. The same procedure does not apply using compound III.

The spectrophotometric curves from which the data of Table II were compiled were identical in composition to those of Fig. 3 in which case cobalt was present.

The application of terosole in the determination of iron in both vegetable and chrome-tanned leather has been developed and the description of the procedure accompanied by experimental documentation will be the subject of a separate investigation.

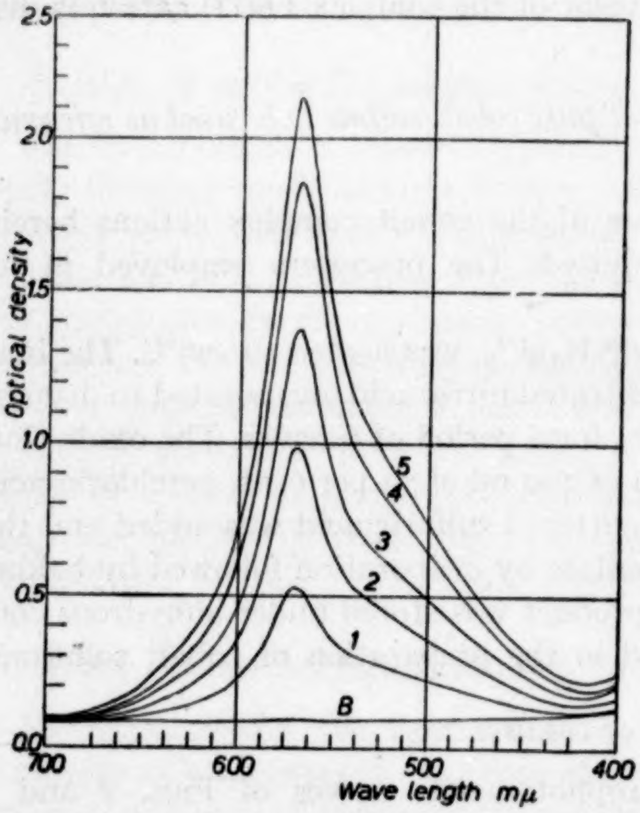

Fig. 3. Determination of iron in presence of cobalt using terosine

1 0.0176 mg Fe; Co none
2 0.0261 mg Fe; Co 0.1134 g
3 0.0361 mg Fe; Co 0.1059 g
4 0.0445 mg Fe; Co 0.1071 g
5 0.0487 mg Fe; Co 0.1065 g
B no Fe Co 0.1063 g

TABLE II

THE DETERMINATION OF IRON IN THE PRESENCE OF COBALT EMPLOYING TEROSINE AS LIGAND AND ETHYLENEDIAMINE AS MASKING AGENT

(1 g of iron solution = 0.1172 mg of iron. 1 g of cobalt solution = 0.117 mg of cobalt)

Iron taken Solution g	Iron taken Fe mg	Cobalt taken Solution g	Cobalt taken Co mg	Optical density 569 mμ	Iron found mg
0.1499	0.0176	none	none	0.681	0.0180
0.2225	0.0261	0.9620	0.1134	1.101	0.0277
0.3084	0.0361	0.8983	0.1059	1.508	0.0379
0.3801	0.0445	0.9084	0.1071	1.850	0.0465
0.4155	0.0487	0.9039	0.1065	2.750	0.0511
None	None	0.9020	0.1063	—	—

SUMMARY

Terpyridine (2,6-bis-(2-pyridyl)-pyridine) and two alkyl substituted analogues of terpyridine have been investigated as organic complexing agents for use in spectrophotometry. Terosine (2,6-bis-(2-pyridyl)-4-phenyl-pyridine) and terosole (2,6-bis-(4-methyl-pyridyl)-4-phenyl-pyridine) were the terpyridine analogues herein investigated.

The determination has been made of the molecular extinction coefficient *E*, and the wavelength of maximum absorption λ_{max}, of the three ligands terpyridyl, terosine and terosole both for the Fe(II) and the Co(II) chelation. The effect of substitutions in the 4,4′, 4″ carbon position of terpyridine on the values *E* and λ_{max} has been shown.

The unsubstituted terpyridine is not extracted from aqueous solution when complexed with either Fe(II) or Co(II), but in the case of terosine the complex may be extracted from aqueous solution by the multiple treatment by *n*-hexyl alcohol. With terosole the colored complex becomes extractable by this immiscible solvent in one operation.

Interfering cations and anions are Cu(I), Ni(II), Co(II), F^-, and ClO_4^-. A procedure is given preventing interference from Co (II) through the use of ethylenediamine as masking reagent for Co(II) when using terosine to complex Fe(II). The ClO_4^- interference results from the formation of a very highly insoluble terosole perchlorate.

Ions which may be present to the extent of 100 mg without interference are Mn(II), Al, Cr(III), the alkali and alkaline earth metals and Mg, PO_4^{-3}, $P_2O_7^{-4}$, $C_2O_4^{-2}$, Cl^-, NO_3^-, Ac^- and SO_4^{-2} among others.

Terosole is the most sensitive iron reagent so far described having an *E* value of 26300 at wavelength of maximum absorption 575 mμ.

RÉSUMÉ

La terpyridine (2,6-bis-(2 pyridyl)-pyridine) et deux de ses dérivés, la terosine (2,6-bis-(2-pyridyl)-4-phényl-pyridine) et le terosole (2,6-bis-(4-méthyl-2-pyridyl)-4-phényl-pyridine) ont été étudiés comme réactifs complexants, en spectrophotométrie.

Les déterminations du coefficient moléculaire *E* et de la longueur d'onde de l'absorption maximum λ_{max} ont été effectuées pour les 3 liaisons terpyridyle, de la terosine et du terosole avec Fe(II) et Co(II). L'effet des substitutions (en position 4,4′ et 4″ de la terpyridine) sur les valeurs de *E* λ_{max} et de a été étudié.

Les complexes de Fe(II) et Co(II) avec la terpyridine non substituée, en solution aqueuse, ne sont pas solubles dans l'alcool *n*-hexylique, contrairement aux complexes du terosole.

Les ions gênants sont: Cu(I), Ni(II), Co(II), F^- et ClO_4^-. On propose une méthode permettant de masquer le cobalt au moyen d'éthylènediamine lors de la formation du complexe terosine-Fe(II). L'ion ClO_4^- gêne car il forme un perchlorate de terosole extrêmement peu soluble.

Les ions suivants (jusqu'à 100 mg) ne gênent pas: Mn(II), Al, Cr(III), les métaux alcalins et alcalino-terreux ainsi que Mg, PO_4^{-3}, $P_2O_7^{-4}$, $C_2O_4^{-2}$, Cl^-, NO_3^-, Ac^- et SO_4^{-2}.

Le terosole est le plus sensible des réactifs du fer, il présente une valeur de *E* de 26300 à la longueur d'onde de 575 mμ (maximum d'absorption).

ZUSAMMENFASSUNG

Die Verwendung von Terpyridin (2,6-Bis-(2-pyridyl)-pyridin) und von zwei analogen alkylsubstituierten Terpyridinen als komplexbildende Reagenzien in der Spektroskopie wurde untersucht. Die beiden in dieser Arbeit untersuchten analogen Terpyridine waren Terosin (2,6-Bis-(2 pyridyl)-4-phenyl-pyridine) und Terosol (2,6-Bis-(4-methyl-2-pyridyl)-4-phenyl-pyridine).

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Es wurden der molekulare Extinktionskoeffizient *E* und die Wellenlänge des Absorptionsmaximums λ_{max} der drei Liganden Terpyridyl, Terosin und Terosol mit Fe(II)-und Co(II)-Chelation bestimmt. Der Effekt der Substitution in den 4,4′ und 4″ Kohlenstoffstellungen des Terpyridins auf die *E*-und die λ_{max}-Werte wurde gezeigt.

Das unsubstituierte Terpyridin kann aus der wässrigen Lösung, wenn es von Fe(II) oder Co(II) komplex gebunden ist, nicht extrahiert werden; beim Terosin jedoch kann der Komplex durch wiederholtes Behandeln mit *n*-Hexylalkohol aus der wässrigen Lösung extrahiert werden, während bei Teresol der gefärbte Komplex mit diesem nicht mischbaren Lösungsmittel in einer Operation extrahiert werden kann.

Störende Kationen und Anionen sind Cu(I), Ni(II), Co(II), F^- und ClO_4^-. Es wird ein Verfahren gegeben, das bei der Verwendung von Terosin zur komplexen Bindung von Fe(II) das störende Co(II) mit Äthylendiamin maskiert. Die Störung mit ClO_4^- wird durch die Bildung eines äusserst unlöslichen Teresolperchlorats verursacht.

Ionen, die bis zu einem Ausmass von 100 mg vorhanden sein können ohne eine Störung hervorzurufen, sind u.a. Mn(II), Al, Cr(III), die Alkali- und Erdalkalimetalle, Mg, PO_4^{-3}, $P_2O_7^{-4}$, $C_2O_4^{-2}$, Cl^-, NO_3^-, Ac^- und SO_4^{-2}.

Teresol ist von den bisher beschriebenen Eisenreagenzien das empfindlichste; es zeigt bei 575 mμ (Wellenlänge der maximalen Absorption) einen *E*-Wert von 26300.

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A CRITICAL EVALUATION OF COLORIMETRIC METHODS FOR THE DETERMINATION OF PLATINUM METALS

by

F. E. BEAMISH AND W. A. E. McBRYDE

University of Toronto, Toronto, Ontario (Canada)

For a period of about one hundred years the analytical separation of the platinum metals and gold from ores has involved recovery en masse by the process known as fire assay. Subsequent separations and determinations were generally made by classical methods. From time to time the wet treatment of ores has been proposed, but in no case has the efficiency of recoveries been determined. Indeed such proof would require comparisons with fire assay methods whose validity also remains in doubt.

During the past decade two new approaches to the problem of separation of platinum metals from each other have been proposed. Each of these will facilitate the examination of the efficiency of older methods and indeed may replace them. One process involves the use of selective extractions and the other, specific adsorption. In many cases these separations are especially suited to subsequent determination by colorimetric methods, the number of which have increased to a degree that critical evaluation is now desirable. Furthermore, many of the older visual methods have been converted to spectrophotometric methods and it will be useful to have all of these procedures placed in better perspective.

No attempt is made here to assign credit for the discovery of any color reagent or to record the progress in the application of the reagent from qualitative to quantitative purposes. Nor do the authors evaluate the rather numerous color reactions which may sometime become the basis for improved colorimetric methods. Of those published to date most of the color reactions involve reagents which have been used qualitatively for many years. For each metal there are recommended colorimetric methods which are considered superior. Particularly, an effort is made to suggest the most advantageous areas of application of colorimetric methods. There is evidence that some investigators in this field have sponsored their specialty to a degree that wider usefulness has been sacrificed.

Concerning the references to interfering cations the authors have been guided by the fact that, with the exception of iridosmines, the most important natural deposits contain platinum and palladium as major constituents with rhodium, iridium, ruthenium and osmium as minor constituents. Of the non-platinum metals the associated cations are generally the base metals of Column VIII and chromium. In the case of artificial products platinum, palladium and, less frequently, rhodium are major constituents. In addition there are the hardening metals iridium and ruthenium, which are sometimes added in appreciable proportions. Other interferences arise from the various anions peculiar to the preliminary methods of separation. Little attention is paid to freedom from interference by proportions of associated metals which are seldom encountered in practice. Furthermore it should be noted that interference from one platinum metal may vitiate the advantages gained by non-interference from another. For example if palladium and osmium interfere with the determination of ruthenium there is little advantage in freedom from interference by rhodium and platinum.

With respect to the optimum range of concentrations, it is generally agreed that for maximum precision in photometric work it is desirable to operate with the optical density neither too great nor too small. When Beer's law applies and a "blank" is used to set the zero reading on the optical density scale the relative uncertainty in a determination of concentration is a known function of the uncertainty in the measurement of transmittancy, *viz.*

$$\frac{\mathrm{d}c/c}{\mathrm{d}T} = \frac{0.4343}{T \log T}$$

The quantity on the right hand side of this equation attains the value 5 at optical densities 0.112 and 1.10 and increases rapidly as one passes outside these limits. The authors have felt that it was desirable to prescribe ranges of concentration within which the procedures described would be most precisely applicable. The ranges of concentration which appear in what follows are frequently those which yield the afore-mentioned optical densities when 1 cm cells are used. However, in some cases narrower ranges than these are suggested when the available data are insufficient to permit extrapolation, or when precipitates are known to form; in such cases the ranges are designated by an asterisk.

PLATINUM

Excluding methods of separation by fire assay the most generally useful procedure for the isolation of platinum is that perfected by GILCHRIST[1]. This method involves the removal of base metals as hydrated oxides from the nitrite complexes of the platinum metals. The platinum metals are then converted to the higher oxidation states and all but platinum removed as the hydrated oxides. Recently, processes involving selective solvent extractions have been used with some success. Platinum thus isolated may be determined by a variety of methods, but for amounts less than 1 mg the classical methods are not applicable. These small amounts, encountered frequently in practice, are in general best determined by spectrographic or colorimetric methods. Only three color reagents have been applied with success, tin (II) chloride, potassium iodide and thiosemicarbazide. Of these the first reagent is recommended.

Probably the most serious objection to potassium iodide is the ease of oxidation of acidified iodide solutions. The dissolving of platinum is usually accomplished by oxidizing reactions, and care must be taken to eliminate all residual oxidizing agents before the color reaction is carried out. Potassium iodide reacts with several of the platinum metals as well as with many of the associated metals, for instance lead or iron.

Perhaps the first author to deal quantitatively with the colorimetric determination of platinum by potassium iodide was MINGAYE[2] who used the method to determine platinum in sands. Visual comparisons were made against freshly made standards; depositions occurred in aged standards. MINGAYE concluded that "The method is simple, easily performed, accurate, and enables a large number of estimations or checks to be put through in a comparatively short time".

ARDAGH, SEABORNE AND GRANT[3] who have presented the best exposition of the iodide method stated "the method is not by any means so simple and so free of pitfalls as MINGAYE declares it to be". They found that, for the optimum concentration of 2-4 p.p.m., full color development was attained only after 16-18 hours standing at room temperature, although the color intensity developed by one hour's standing approximated 90% of the maximum. Heating the solution to 40° before the addition of potassium iodide hastened the development of color, but heating to temperatures near boiling prevented color development. Color once developed was not easily destroyed. Aged solutions of chloroplatinates developed color more rapidly than freshly prepared solutions. Heating to 50° after addition of the iodide caused a rapid development of color which however did not reach the maximum obtained at room temperature. Prolonged heating of solutions containing 1 p.p.m. at 50° C produced colorless solutions, and with stronger solutions considerable fading of color. Addition of excess reagent or exposure to sunlight was without effect. Because associated metals including gold, silver, copper, nickel, etc. interfered, various procedures were provided to isolate platinum. With the exception of hydrochloric acid, the shade, intensity, and rate of color development were affected adversely by mineral acids.

SANDELL in his discussion of the iodide method[4] stated that a high acidity was undesirable because of the increased tendency to form iodine. Oxidizing impurities must be absent as well as palladium, gold, iron, copper and bismuth. The range of concentration recommended was 0.5-6 p.p.m.* Minimum transmission occurred about 490 mμ and a blue-green filter was recommended. The color intensity increased gradually at room temperature. SANDELL recommended color development in the dark for a period of one hour.

The present authors have found Beer's law applicable up to at least 14 p.p.m. when optical density is measured in a Beckman spectrophotometer at 495 mμ. The most suitable range of application lies between 1.8 and 18 p.p.m. Moderate concentrations of sodium chloride interfered.

KARPOV AND SAVCHENKO[5] recorded a comparative evaluation of the potassium iodide and tin (II) methods. They stated that in the former method the color was fully developed in one hour, whereas fifteen minutes sufficed in the latter. Considerable data were supplied from which they derived the optimum concentration ranges of the two procedures. They concluded that the iodide method made possible determinations over a wider range than the tin (II) chloride procedure. For the iodide method the optimum range was 1-8 p.p.m.*, and for the tin (II) method the range was 1-2 p.p.m.* Within these ranges the smallest relative error in the determination of known amounts of platinum was found, and the accuracy of the two methods was about the same, namely 3-4%. The concentrations quoted are based upon the inference that these authors were diluting all samples to a volume of 50 ml. These authors assumed that the colored constituent produced by tin (II) chloride was due to bivalent platinum and they concurred with DAVIS[6] who stated that the color was inversely proportional to the concentration of the hydrochloric acid solution.

Probably the earliest application of tin (II) chloride to the colorimetric determination of platinum was made by DAVIS[6]. Visual comparisons were made over the concentration range 2.5-100 p.p.m. The full intensity of the color developed within 10 or 15 minutes and remained unchanged for several hours. Preliminary to the determination, platinum was precipitated, isolated, converted to a salt, and finally dissolved in hydrochloric acid. For amounts of platinum less than 0.2 milligrams the colorimetric method yielded more accurate results than the gravimetric method but for larger amounts the reverse was true.

WÖLBLING[7] added tin (II) chloride to ammonium chloride solutions of platinum, palladium, rhodium and iridium and subsequently extracted the platinum with ethyl acetate. However the procedures are qualitative in nature and no data are provided.

SANDELL[8] used the tin (II) chloride method for samples containing 0.5-2 p.p.m. The color intensity depended upon the hydrochloric acid concentration and a final acidity of about 0.25*N* was recommended. The color development was very rapid and the color remained stable. Of the platinum metals palladium provided the greatest interference. Ruthenium interfered to a lesser degree and rhodium, iridium and gold in low concentrations did not interfere seriously. Small quantities of iron and copper did no harm. Reference was made to the fact that "chloroplatinous acid" could be isolated by extractions with ether and with ethyl alcohol from 1*N* solutions of hydrochloric acid.

In a report of the spectrophotometric study of the tin (II) method, AYRES AND MEYER[9] set out in good detail the various factors which affect the accuracy of determination of platinum. They reject the possibility that the colored constituent is attributable to either chloroplatinous acid or bivalent platinum. As evidence against the latter they record the results of an experiment with tin (II) sulfate and a solution of platinum obtained by fuming with sulfuric acid. In this connection it may be recalled that the platinum thus prepared cannot be isolated quantitatively by oxidation and subsequent hydrolytic precipitation, hence the implication by these authors may be invalid. AYRES AND MEYER also found that when the amount of concentrated hydrochloric acid was greater than 6 ml per 100 ml of final solution there was little change in transmittancy. The optimum range measured at 403 mμ was 3-25 p.p.m., and could be extended through the use of platinum reference solutions to about 70 p.p.m. The colored constituent in aqueous medium was stable indefinitely, was little affected by temperature, and the effect of heating was reversible. The optimum amounts of the reagents tin (II) chloride and ammonium chloride were not critical. An extensive investigation of interferences was made involving the usually associated constituents. Serious interference was encountered in the case of rhodium and palladium. A method of selective extraction with amyl acetate was described and the factors which adversely affected the extraction were discussed at some length. While the proposed procedure for separation will find uses in specific instances the method is not a good one. Apparently no consideration was given to the probable advantageous application of GILCHRIST's separation[1] which, by oxidation with bromate and subsequent hydrolysis, will isolate platinum from all of the remaining platinum metals. The incorporation of this procedure may greatly improve the usefulness of the tin (II) method.

For higher concentration ranges, 10-90 p.p.m., DE TRECCO[10] used thiosemicarbazide to produce a blue solution which obeyed Beer's law. The color was developed in a sodium acetate medium after one hour's standing at room temperature. Extractions could be made with acetic esters and amyl alcohol or an alcoholic solution of chloroplatinic acid could be used directly. Measurements of the stable color were made with a red filter. The author did not deal with interference, and included no data concerning the accuracy of the method. Undoubtedly this reagent should be subjected to further investigations.

PALLADIUM

Palladium is one of the major constituents in both naturally occurring and prepared platinum metal products. Its separation is the most easily effected of all these metals and its determination in either large or small amounts by classical methods may be accomplished with considerable ease and with good accuracy. Consequently in normal analytical practice colorimetric methods would seem to have relatively little application. However, where the direct assay of ores is required the amount of platinum metals collected rarely exceeds one milligram and the more sensitive methods are needed. In addition there are many instances, particularly in the field of research, where the analyst is required to determine traces of palladium.

The reagents so far applied to the colorimetric determination of palladium are *p*-nitrosodiphenylamine, *p*-nitrosodiethyl- and *p*-nitrosodimethylaniline; 2-mercapto-4:5-dimethylthiazole; 1-nitroso-2-naphthol; 2-nitroso-1-naphthol; *p*-bromaniline; bromide ion; and tin (II) chloride.

YOE AND OVERHOLSER[11] used *p*-nitrosodiphenylamine which is the most sensitive reagent for the colorimetric determination of palladium. The colored constituent is a coordination compound of the composition $Pd(C_6H_5NHC_6H_4NO)_2Cl_2$, yielding a red solution under the conditions recommended. The reagent can only be used with a sodium acetate-hydrochloric acid buffer and little variation from the optimum pH of 2.1 is permissible. The concentration range is 0.05-3 p.p.m. Measurements may be made by photoelectric colorimeter but the Duboscq colorimeter cannot be used. The effectiveness of the method is reduced by the deleterious effect of salts, the interference of oxidizing reagents and of gold. The latter may be isolated by solvent extraction. Silver and large proportions of platinum also interfere and must be removed. The effects of platinum and rhodium on determinations made with this reagent have also been discussed by RYAN[12]. In a later paper, OVERHOLSER AND YOE[13] provide a useful procedure for the determination of palladium in the presence of silver by color development with *p*-nitrosodiphenylamine in a nitrate medium. They also compare the effectiveness of this reagent with *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline. These two reagents possessed advantages over the former because of a faster reaction rate, greater stability of color and smaller temperature effect. The present authors have found the above methods useful where traces of palladium were determined.

For the determination of palladium within the range 0.5 to 8 p.p.m. RYAN[14] used 2-mercapto-4:5-dimethylthiazole. This method is not sensitive to variations in acidity or salt content and only platinum interferes. To separate the latter the usual hydrolytic separation is used. If necessary palladium can be isolated by an ethyl acetate extraction of the palladium diphenylamine complex. Subsequently the organic matter must be destroyed before treatment with the dimethylthiazole reagent. This separation is unnecessarily cumbersome. Although the method has the advantage that gold does not interfere except in large proportions the obvious disadvantage is the interference of platinum which is the almost constant companion of palladium. The effective concentration range allows for some application to the analysis of assay beads and buttons. It should be noted however that when sulfuric acid is used as a parting acid the hydrolytic method of separation from platinum is inadmissable.

Two sensitive reagents for palladium, one of which has been used for gravimetric determination, were recorded by ALVAREZ[15]. The orange colored toluene extracts of palladium 1-nitroso-2-naphtholate $[C_{10}H_6O(NO)]_2Pd$ could be applied colorimetrically over the concentration range of 0.5 to 5 p.p.m.* The color intensity was greater for extractions made from neutral or weakly acid solutions than from strong acid or alkaline media. The complex was stable in acid concentrations of 1.5 normal and partially destroyed in strong acid or alkaline solutions. The excess reagent was also extracted with toluene, but could be removed by the addition of sodium hydroxide to the colored solution without affecting the palladium complex. Although the stability of the colored constituent in toluene was reasonably good the color faded with time, more rapidly if the extraction was made from strongly acidic solutions. The maximum absorption of light was obtained with a broad band filter at 420 mμ, and the solutions obeyed Beer's law. No data were included concerning interferences from other platinum metals; however, in the gravimetric field this reagent has been recognized as acceptably specific. The author provided a modified procedure to deal with the interferences from copper and chromium. Nickel interfered slightly and cobalt and iron interfered, although ferric iron could be eliminated by sodium fluoride. There was less interference when 2-nitroso-1-naphthol was used and this reagent, whose toluene extract was a violet color, appeared to have a greater qualitative sensitivity. Undoubtedly these two reagents merit more detailed study.

RICE[16] described an interesting method for the concentration range 2.4-6 p.p.m.* Palladium was precipitated by β-furfuraldoxime; the precipitate was isolated by centrifuging, dissolved in glacial acetic acid and *p*-bromoaniline was added. The solution was heated to 70° for exactly five minutes, cooled for 2-3 minutes in cold water and after standing 55 minutes at room temperature the optical density of the pink solution was measured at the transmittancy minimum of 520 mμ. Attempts to precipitate less than 12 micrograms of palladium gave erratic results while amounts greater than 60 micrograms introduced mechanical difficulties. Beer's law held over the recommended range. The maximum color was reached in 50 minutes, remained constant for 25 minutes, then faded. The author did not identify the colored constituent but it is possible that the color is due to a reaction between the bromoaniline reagent and furfuraldoxime. In any case these reagents do produce a pink color. Obviously this method suffers from the disadvantage that all cations precipitated by the oxime and soluble in acetic acid would interfere and furthermore excess of precipitating reagent must be removed. The author records no data concerning interference from other platinum metals. However furfuraldoxime resembles dimethylglyoxime with respect to specificity and undoubtedly interference could be reduced by adjustments of the acidities of the precipitating media. Gold interferes to the degree that the metal is produced by the reagent and must be removed prior to the measurement of color.

For the concentration range of 37-360 p.p.m., AYRES AND TUFFLY[17] recommend the spectrophotometric determination of palladium as bromide. It will be noted that within this range and beyond it gravimetric and volumetric methods have been proposed. The authors recommend the spectrophotometric method because "gravimetric separations and determinations are time-consuming, and are liable to be subject to errors such as incomplete precipitation and co-precipitation of other elements". Aside from the fact that this statement is misleading the best of the three procedures proposed by the authors, which involves the formation and extraction of palladium-phenylthiourea, will not in general yield the accuracy of several gravimetric methods. Moreover it is questionable that even single determinations by this procedure, involving as they do the destruction of organic matter and treatments with aqua regia and hydrochloric acid, can be made more rapidly than gravimetric determinations. The interference of sulfuric acid eliminates application of the method to the analysis of assay beads when the latter are parted by sulfuric acid. However the procedure provides a colorimetric method for those who desire to use these methods for the higher ranges of concentration. With some modification the method may find application to the analysis of platinum metal concentrates.

It is a surprising fact that relatively little use has been made of the color reaction between tin (II) chloride and palladium. KNYAZHEVA[18] used this reagent in a method for the determination of palladium and platinum in silver products. The procedure involved the simultaneous extraction by ether of the reaction product of tin (II) chloride with palladium and platinum, and destruction of the palladium color by sodium hypophosphite. Platinum was then determined by visual colorimetry. Solutions for comparison, containing the amount of platinum thus ascertained, were prepared by adding palladium to match the color of the original platinum-palladium solution. The pink color of the palladium complex was stabilized by copper (II) chloride and although silver chloride was formed it did not interfere. At best this method would be useful in a very restricted field. Color comparisons could not be made by artificial light and the method is subject to all of the difficulties inherent in methods of determination by difference. Data pertinent to KNYAZHEVA's method, are provided by AYRES AND MEYER[9] whose spectrophotometric method for platinum is discussed above. These authors used amyl acetate to extract the colored constituents formed by tin (II) chloride in solutions containing platinum and palladium. They found that the amount of palladium extracted depended upon the concentrations of hydrochloric acid and tin (II) chloride. Interference by the palladium in the extract increased up to concentrations of 5 p.p.m. and then remained constant up to a concentration of 50 p.p.m. Consequently, to avoid interference with the tin (II)-platinum system, they proposed a deliberate adjustment of the palladium content to fall within this range.

Reference should be made here to a method developed by ROBINSON[19] which depends upon the assumption that "the depth of (the) yellow to brown color imparted by palladium to the sulfuric and nitric acids from the parting of the beads in the usual way, when conducting a gold, silver, and platinum assay, was proportional to the quantity of palladium present, other conditions being alike". This method is not recommended because in the fire assay conditions are seldom sufficiently alike. Furthermore the range of application is high, the accuracy is not good, and most of the methods described above are superior from every point of view.

IRIDIUM

The separation and determination of iridium enjoys the distinction of being the most difficult procedure in the analyses for platinum metals. There are no reagents for the gravimetric determination of iridium which even approach specificity and furthermore there are no published methods for the quantitative separation of small amounts of iridium from rhodium. The macro method involving separation of rhodium by titanium (III) which is subsequently removed by cupferron is by no means applicable. Unfortunately few colorimetric methods for the determination of iridium have been proposed. Of the methods published only one has been developed to the point where it is generally useful. The remaining procedures involve the use of an iridium salt to produce, by oxidation, a colored organic compound. Obviously this type of procedure is subject to the objection that many of the reagents used in platinum metal analyses are oxidizing in nature and hence will interfere. Furthermore these procedures are incompletely developed and in their present form will provide little more than semi-quantitative data.

The single available method was developed by AYRES AND QUICK[20] and involves the production of a purple color through the use of a mixture of perchloric, phosphoric and nitric acids. The identity of the purple dissolved constituent has not been determined although some progress toward identification has been made. Transmittancy measurements are made at 564 mμ on solutions of iridium containing from 8 to 80 p.p.m. over which range there is good agreement with Beer's law. From the view point of interference the method is a particularly good one. During the preparation of the colored constituent both osmium and ruthenium are volatilized; in concentrations of 200 p.p.m., iron, cobalt, nickel, and platinum do not interfere. Although rhodium and palladium are precipitated initially these metals are dissolved in the final solution. The latter is tolerated up to about 80% of the iridium content.

Unfortunately the present authors' experience with this procedure has not been entirely satisfactory. Measurements with a Lumetron Model 402E colorimeter with the so-called monochromatic filter No. M560, upon replicate samples prepared rigorously by the procedure of AYRES AND QUICK showed a most discouraging average deviation. The authors have also noted that iridium samples containing sulfuric acid cannot be compared with standards which contain none of this acid, so that the latter must be added in comparable amounts to each standard.

The color of red-brown ammonium hexachloroiridate (IV) was used by KHLOPIN[21] to determine the proportions of iridium in solutions of ammonium hexachloroplatinates. Among the obvious disadvantages are lack of specificity and sensitivity.

RHODIUM

In all known commercial deposits of the platinum metals rhodium is present in relatively small proportions. The usual wet treatments of the fire assay beads or buttons yield an insoluble residue which in many cases contains small amounts of rhodium and iridium. As stated above the separation of these metals is not a simple process. The amounts present are practically always small, generally less than 0.1 mg. Of the two metals rhodium is the more easily determined since it can be isolated relatively free of impurities.

A serious defect of all but one procedure published to date is the absence of data concerning the color development in solutions of rhodium prepared by boiling in sulfuric acid, which is the only wet reagent capable of dissolving this metal. Furthermore, in the assessment of interfering reagents the questionable assumption is too often made that the complexity of the dissolved platinum salt is immaterial. In this connection one need only to recall the very appreciable difference in ease of oxidation of dissolved chloro and bromoruthenates.

For the range 1-8 p.p.m.*, 2-mercapto-4:5-dimethylthiazole is a useful reagent. RYAN[22] isolated the colored constituent and suggested the formula $(C_4H_6NSCS)_3Rh$. The maximum color development was obtained by boiling for one hour in concentrated hydrochloric acid solutions. The amber-to-red solutions obeyed Beer's law and were stable in daylight for at least 48 hours. Measurements were made with filters whose maximum transmittancy was 430 mμ. There was no appreciable interference from iron, cobalt, nickel or the various anions associated with the determination. Platinum and gold interfered only to the degree that under the experimental conditions used they yielded precipitates. The filtrates however were free of interference. Although palladium must be removed, colorimetric determinations could be made directly with the dimethylglyoxime filtrate. The not inconsiderable defect of the method lies in the interference of iridium. The author suggested that "if the amount of iridium present is known the interference can readily be compensated for". However, "you must first catch your hare", and there are no published methods for determining small amounts of iridium in the presence of rhodium. In a second publication the author[23] applied the above reagent to solutions of rhodium prepared by boiling with sulfuric acid. However the value of this extended application is reduced by the interference from iridium.

For the range of concentration 2-10 p.p.m. the reagent 2-mercaptobenzoxazole is applicable. RYAN[24] precipitated rhodium by this reagent and dissolved the insoluble red complex in acetone to produce a yellow-to-red, stable solution. Although maximum absorption occurred in the ultraviolet, measurements were made with a blue filter (maximum transmittancy at 420 mμ). The solution did not obey Beer's law. The platinum metals which interfered most strongly were platinum and palladium. This procedure may prove useful for the determination of rhodium following its separation from iridium by titanium (III) chloride because small proportions of iridium do not interfere.

For the range of concentration 3-29 p.p.m. tin (II) chloride is a useful reagent. IVANOFF[25] used this reagent for the determination of rhodium by visual comparison. To remove impurities the authors fused the impure sample with potassium hydrogen sulfate and extracted with water. BOUVET[26] modified IVANOFF's procedure by introducing sodium chloride to the potassium hydrogen sulfate fusion. The rose color was developed by heating in a water bath for 15 minutes and subsequently cooling for a minimum of one hour. The rose colored solution did not obey Beer's law. A second less sensitive method was also used. This involved the direct measurement of the rose color produced in the aqueous solution of the fusion without the addition of tin (II) chloride. The procedures were applied to the determination of colloidal solutions of rhodium and no data concerning interferences were recorded. In a review of methods for the separation and determination of platinum metals SINGLETON[27] included a brief recipe for the determination of rhodium by tin (II) chloride. The sensitivity is given as 1 p.p.m., but the procedure is insufficiently developed and the proposed method of isolation of rhodium is unacceptable. SANDELL[28] stated that either the red color, developed in 2 *N* hydrochloric acid or the yellow form, occuring in less acid media, could be used for colorimetric purposes. The former was preferable for larger amounts of rhodium. While the latter was more sensitive it was also less accurate, and careful control of chloride concentration and time of standing was necessary. It should be noted here that MCBRYDE AND YOE[29] were unable to obtain precise results with the yellow form. For this form SANDELL recommended a period of one hour at room temperature for color development, measurements being made with a blue filter (435 mμ). For the red form, transmittancy measurements could be made without delay with a green or blue filter (480 mμ). The rhodium complex could also be extracted from strong hydrochloric acid solutions with ethyl acetate to produce a yellow solution. Other platinum metals interfered, particularly platinum and palladium. The red form has been used in the authors' laboratory for many determinations of rhodium. After heating, the solutions were diluted with 2 *N* hydrochloric acid. When measurements were made with a Beckman spectrophotometer, Beer's law was found to hold up to 40 p.p.m. at a wavelength of 480 mμ.

For the concentration range 3.5 to 34 p.p.m. the reagent sodium hypochlorite may be applied. AYRES AND YOUNG[30] recorded a spectrophotometric study of the blue color developed by this reagent in rhodium solutions whose pH ranged from 4.7 to 7.2. Delay in adding hypochlorite to the buffered rhodium solution resulted in solutions less intense in color. However good reproducibility was obtained after one hour when the reactants were added in rapid succession regardless of the order of addition. The colored solution obeyed Beer's law and had a transmittancy minimum at 665 mμ. To produce the maximum blue color a high ratio of hypochlorite to rhodium was required. The colored constituent was not identified. The method tolerates considerable proportions of platinum and especially palladium. The latter, with hypochlorite, produces a visible color which does not influence appreciably the transmission at 665 mμ. The method is not free from interference. Certain base metals such as copper and cobalt interfere if present in proportions about equal to rhodium. The most serious interference occurs with iridium.

MYLIUS AND MAZZUCHELLI[31] discussed briefly the possibilities of colorimetric determinations of platinum metals in strong hydrochloric acid solutions. No procedure is offered and in the opinion of the authors the method has little to commend it.

For the determination of rhodium in platinum alloys RYABCHIKOV[32] converted the metals to hexachloro- salts and decolorized the yellow platinum salt with potassium hydrogen sulfite. Rhodium was determined in the Dubosq colorimeter by comparison of the pink color with standard solutions. No data were included to support the high accuracy claimed for the method. A procedure, of similarly restricted value, was recorded in United States Patent, No. 2,085,177 (1937) by ZSCHIEGNER[33]. Solutions of substantially pure rhodium were treated with bromide and color comparisons made with standards. Methods such as these suffer from lack of specificity and sensitivity.

OSMIUM

Colorimetric methods are especially useful for the determination of osmium. This metal is present only as a minor constituent in most platinum metal occurrences and it is seldom used in artificial alloys. The one important osmium mineral, iridosmine, is an exceedingly hard alloy used for phonograph needles, etc., until to some degree replaced recently by synthetic materials. However osmium is frequently present as a trace constituent in the final "insoluble" resulting from wet treatments of assay buttons and beads. Osmium compounds are also used as catalytic reagents and in all these cases sensitive methods of determination may be required. No methods of any kind are available for the determination of osmium in the presence of all the remaining platinum metals. Fortunately nature has provided an easy method of isolation. Although a large number of oxidizing reagents may be used to produce the volatile octavalent oxide, all but one of these will also yield the corresponding ruthenium compound. Nitric acid is the only specific reagent for this reaction and of course there is the disadvantage that this acid must be removed from the distillate before determinations can be made. It is expected that more suitable specific oxidants will soon be recorded. Although sodium hydroxide solution is the most efficient collecting liquid for both osmium and ruthenium, the hydrochloric acid-sulfur dioxide medium is more generally applicable to the various methods for determining osmium.

The reagents used for colorimetric determination are: thiourea, and a variety of oxidizing reactions catalyzed by osmium in which the amounts of osmium are correlated with the rate of oxidation.

For very low concentrations of osmium a series of four methods, all similar in principle have been proposed by SHIOKAWA[34]. These procedures involve measuring the increase in the rate of various oxidizing-reducing reactions caused by increasing amounts of osmium salts. The reagents with their approximate ranges of application are potassium chlorate and potassium iodide, 0.02-0.2 p.p.m.*; phenylenediamine and hydrogen peroxide, 0.04-0.2 p.p.m.*; ceric sulfate and arsenic (III) oxide, 0.01-0.06 p.p.m.*; potassium permanganate and arsenic (III) oxide, 0.08-0.38 p.p.m.* Various factors such as temperature, acidity, concentration of reagents, and certain anion and cation impurities affected the rate of color change, hence each method requires rigid calibration. The influence of other platinum metals was not reported, however, since isolation of osmium by distillation is required for all known methods, these procedures may well find many useful applications.

Without doubt the most useful procedure for the colorimetric determination of osmium involves the development of the pink thiourea complex. The reagent was first proposed by TSCHUGAEFF[35] who described the reaction as specific and sensitive to 0.1 p.p.m. The composition of the colored complex was given as $Os(NH_2\text{-}CS\text{-}NH_2)_6Cl_3.H_2O$. Sulfur dioxide was used to eliminate the interference from nitric acid which reacted with thiourea. Under the new experimental conditions the limit of sensitivity was recorded as 0.2 p.p.m. The color developed quickly and remained stable. Later, SANDELL[37] used thiourea for the colorimetric determination of traces of osmium in meteorites. The octavalent oxide was distilled and collected in sulfur dioxide-hydrochloric acid. This author observed that evaporation of the distillate resulted in losses of osmium and a procedure was devised that eliminated the evaporations. It was also observed that hexachloroosmate did not produce the colored constituent, consequently in the preparation of standards the octavalent oxide was required. The system was found to obey Beer's law, and could be used over the range of 1-3 p.p.m. Because of the yellow color of thiourea-sulfur dioxide solution, visual methods were less satisfactory than photometric methods. AYRES AND WELLS[38] made a spectrophotometric study of the thiourea-osmium system and recorded a sharp transmittancy minimum at 480 mμ and a less applicable band at 540 mμ. For the former wavelength the optimum concentration range was 5-50 p.p.m. Of the platinum metals only palladium and ruthenium interfered. The latter of course is the more serious interference and makes necessary a selective distillation. It should be noted that these authors used standard solutions prepared from alkaline-osmate solution; and presumably made no distillation of the octavalent oxide. ALLAN AND BEAMISH[39] used HCl-SO_2 receiving liquid and found that the rose complex was formed only with fresh distillates. This fact is also implied in SANDELL's conclusions. Furthermore, the explanation of SANDELL's observation that evaporation of SO_2-HCl-Os distillates resulted in losses of osmium may be found in this same phenomenon. Distillates, left standing at room temperature for some time, could be evaporated without loss of osmium. Difficulties arising out of the presence of sulfur dioxide resulted in the conclusion by ALLAN AND BEAMISH that the more satisfactory receiving liquid contained only thiourea and hydrochloric acid. Complete evaporations were then unnecessary. These authors used the thiourea method for the determination of the losses of osmium by fire assay. A narrow band filter centred at 480 mμ was used and the range of concentration was 0.4-5 p.p.m. It was also observed that the weight of thiourea required for a fixed amount of osmium depended on the volume of the solution. For solutions of osmium of 5 mg per litre overnight standing was advisable to reach the maximum color density. DWYER AND GIBSON[40] used the thiourea reaction to determine osmium in organic compounds. The procedure was devised to avoid distillations since "it has been the experience of the authors and also of others that the recovery of osmium is often of the order of but 90 to 95 per cent. and hence it scarcely can be claimed that this method is sufficiently accurate for quantitative work". No evidence is offered for this statement and to the best of the present authors' knowledge no acceptable evidence has been published. DWYER AND GIBSON record the interesting information that the thiourea reaction may be applied to hexabromoosmate ion. The great discrepancies between the reactions of chloride and bromide complexes of at least some of the platinum metals are rapidly becoming apparent.

RUTHENIUM

Analytical literature contains no procedure which will permit the quantitative determination of ruthenium in the presence of other platinum metals in the proportions normally encountered. Ruthenium together with osmium may be removed by distillation of the octavalent oxides. The latter can then be isolated by distilling with nitric acid. Researches in the authors' laboratory have proved that hydrogen peroxide will permit the selective distillation of osmium from ruthenium and a report of this process will be published in the near future.

Acceptable colorimetric procedures for the determination of ruthenium are more numerous than for any other platinum metal. The reagents thus far proposed are *p*-nitrosodimethylaniline, dithiooxamide, thiourea, 5-hydroxyquinoline-8-carboxylic acid and potassium ruthenate.

For concentrations of ruthenium in the range 0.31-3.1 p.p.m. *p*-nitrosodimethylaniline is a useful reagent. Currah *et al.* applied this reagent to develop a bottle green color in chloride or bromide solution of ruthenium buffered to pH 4.1. Maximum absorption occurred at 610 mμ and the solution obeyed Beer's law. The intensity of the color depended on several factors which required control to produce uniform results. An excess of reagent was necessary and there was a rather narrow optimum range of acidity. In strong acid solutions the color was incompletely developed; in basic solutions the hydrated oxide appeared. Adequate heating was accomplished in 50 minutes at 70° ± 4° C. At higher temperatures there was a tendency to precipitate, at lower temperatures the color development was slower. With the above variables fixed the intensity of color was greater when the volume of liquid heated was decreased. The distillation procedure, used by DeFord[42], was adapted to the determination. There was no interference from sodium or magnesium chlorides or sodium bromide in the amounts usually present. While this reagent is more sensitive than either dithiooxamide or thiourea, within the appropriate range of concentration, the three methods are of comparable value.

For the range of concentration 0.60-5.9 p.p.m. dithiooxamide may be used. Jaffe and Voight[43] determined the composition of the colored constituents. Ruthenium (III) or (IV) produced Ru[SC(NH)CSNH$_2$]$^{+2}$ and Ru[SC(NH)CSNH$_2$]$_3$. Ayres and Young[44] made a spectrophotometric study of the blue color formed by ruthenium chloro-complexes with this compound. Measurements were made at 650 mμ and the solution was found to obey Beer's law. As with thiourea development of the color was accomplished at 85°. A high concentration of acid and a large amount of alcohol were required to prevent the formation of precipitates and to give a stable color. The authors determined the degree of interference of other platinum metals, iron, cobalt, nickel, and various anions which might be present after distillation of ruthenium (VIII) oxide. It should be noted again that the ratios of other platinum metals to ruthenium present in most natural and synthetic products are considerably beyond the tolerances permitted in this method. For this reason and because osmium also interferes, both the thiourea and dithiooxamide methods will find application generally after separations by distillation have been made, and because one cannot, in general, follow the quantitative progress of these distillations, such separations will advisably be "sharp".

An interesting method proposed by Shiokawa[45] for the range 0.7-6 p.p.m.* involves the catalytic effect of ruthenium on the reduction in sulfuric acid media of potassium chlorate by potassium iodide. The author measured the time required for varying amounts of ruthenium to produce sufficient iodine to match a standard acid-Congo red solution. The latter solution is quite stable after two hours standing. Compared to other colorimetric methods this procedure possesses little or no advantage. Very careful standardization will be required and numerous elements including osmium will interfere.

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For the determination of ruthenium in the range of about 2-26 p.p.m., thiourea is a satisfactory reagent. Various authors have made contributions to this method. A qualitative study of the reaction of thiourea and its derivatives was made by STAIGER[46]. JAFFE AND VOIGHT[47] stated that thiourea reduced ruthenium (IV) to ruthenium (III) which subsequently formed the two dissolved constituents $Ru[SC(NH)NH_2]^{+2}$ and $Ru[SC(NH)NH_2]_3$. SANDELL[48] found that the hue and the strength of the color depended to a marked degree upon the acid concentration and recommended an acidity of 4 normal. The color developed rapidly on heating and was moderately stable. However the author stated that turbid solutions appeared with more than 5 p.p.m. ruthenium. In a communication, which unfortunately has not been published, DEFORD[42] used thiourea for colorimetric determinations and introduced new features into the usual procedure for separation. Distillations were made from solutions containing perchloric acid and sodium bismuthate. The necessity of adding the latter reagent was not confirmed. Ruthenium (VIII) oxide was collected in a centrifuge tube containing a solution of sodium hydroxide. Ethyl alcohol was added to produce the hydrated oxide of ruthenium which was subsequently collected by magnesium hydroxide. The mixture was isolated, treated with hydrochloric acid and potassium iodide. The latter reagent prevented the oxidation of thiourea by ruthenium in its higher valency states. The amount of thiourea added could be varied by as much as ± 20%. The optimum acid concentration was 4 normal although considerable excess could be added without changing the optical density of the final solutions. For good reproducibility the time of heating must be controlled accurately. The optimum range of concentration was 2.6-26 p.p.m. AYRES AND YOUNG[44] used this determination for the concentration range 1.9-18 p.p.m. In order to produce quickly a stable color system they recommended an initial 6*N* hydrochloric acid solution, a large excess of thiourea, the presence of 50% by volume of ethyl alcohol, heating for 10 minutes at 85° C and a final solution about 4 normal in acid. Measurements may be made with a band at 620 mμ sufficiently broad to permit the use of filters. Although a sharp absorption band occurred at 305 mμ, the former was preferable from the standpoint of avoiding interferences from associated metals. In view of the fact that the unavoidable interferences were due to cobalt, chromium, palladium and osmium, it would seem that a separation is required in any case. Furthermore, a good separation presents little more difficulty than a poor separation. Although the authors did not apply the method to distillates they determined the influence of the anions which might appear as dissolved constituents in the various media used for receiving ruthenium (VIII) oxide. The most recent report on the thiourea reagent for ruthenium has been recorded by MUSIL AND PIETSCH[50]. Apparently these authors had no knowledge of the previously recorded procedures dealing with this determination. In any case, no reference to the earlier researches are included and nothing original of any importance is recorded. It should be noted that the method of dissolving the metal by fusion in a silver crucible is also not new.

For the range of concentration 2.1-21 p.p.m., BRECKENRIDGE AND SINGER[51] used 5-hydroxyquinoline-8-carboxylic acid. This is one of the two reagents thus far recorded which has been applied to distillates obtained by collecting ruthenium (VIII) oxide in hydrogen peroxide. These greenish distillates are relatively free of interfering constituents and require no evaporations. The procedure involved distillation with perchloric acid, boiling the distillate with hydrobromic acid and subsequent dilution to volume. The aliquots were treated with sulfuric acid, the reagent was added and the solution was boiled, cooled, diluted to volume and transmission readings taken at once. The bluish-black solution obeyed Beer's law and the only sensitive interference occurred with iron. Small proportions of iridium, platinum and osmium did not interfere. This is not a particularly useful advantage in that separation by distillation would generally be required. While this reagent might find satisfactory application there is the difficulty that it is not listed for sale by any of the manufacturers known to the authors.

For the concentration range 6.5-64 p.p.m., MARSHALL AND RICKARD[52] measured the absorbancy of the orange-red potassium ruthenate solutions at 465 mμ. The solution could be stabilized for at least 0.5 hour by adjusting to 2 normal with sodium hydroxide. Like many alkaline solutions of the platinum metals reduction is effected by contact with dust containing organic matter. When large numbers of samples are to be determined and high accuracy is not essential this colorimetric method is superior to gravimetric and volumetric methods. The remaining platinum metals do not interfere if the concentration of each metal is less than one fifth that of ruthenium. This condition however is seldom obtained.

Various other methods of lesser importance have been proposed. ZVYAGINTZEV[53] used the brown K_2RuCl_6 for colorimetric purposes. Following fusion of the sample and distillation of osmium and ruthenium the latter was converted to the chloride complex and the ruthenium determined by visual comparison with standards. The corresponding osmium complex was colorless. The method in its present form is quite inaccurate and subject to numerous interferences. It is not recommended.

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SUMMARY

This paper is a review of quantitative colorimetric methods for the six platinum metals and covers the period up to May, 1953. Each method is evaluated from the point of view of the optimum concentration range, specificity and practical applications to the assay for platinum metals.

RÉSUMÉ

Les auteurs ont fait une étude critique des méthodes colorimétriques quantitatives des 6 éléments des métaux du platine. Cette revue s'étend jusqu'en mai 1953. Chaque méthode est envisagée du point de vue: concentration optimum, spécificité et applications pratiques.

ZUSAMMENFASSUNG

Diese Arbeit ist eine Übersicht der quantitativen kolorimetrischen Methoden der 6 Platinmetalle und erstreckt sich bis zum Mai 1953. Jede Methode wird hinsichtlich ihres optimalen Konzentrationsbereiches, ihrer Spezifität und ihrer praktischen Anwendbarkeit zur Bestimmung der Platinmetalle gewertet.

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THE MICRO-ESTIMATION OF COPPER WITH TRIPHENYLMETHYLARSONIUM THIOCYANATE

by

K. W. ELLIS AND N. A. GIBSON

Chemistry School, Sydney University, Sydney, N.S.W. (Australia)

INTRODUCTION

Triphenylmethylarsonium thiocyanate, in conjunction with an extraction technique, has already been shown to be useful for the colorimetric micro-estimation of iron[1] and cobalt[2], and in this paper its use for the estimation of copper is examined.

Although a large number of reagents have been suggested for the colorimetric micro-estimation of copper[3,4], only dithizone[5,6,7,8] and sodium diethyldithiocarbamate[9,10,11,12] are in general use. Dithizone reacts with a number of metals and usually requires rather tedious separation procedures. Sodium diethyldithiocarbamate gives a compound with copper which can be estimated as a colloidal suspension or extracted with organic solvents. Serious interference, however, is caused by the presence of iron, nickel, cobalt and bismuth, and most metals other than calcium and magnesium interfere to some extent. Most useful among the remaining coloured copper compounds are the chloroform-soluble stable green precipitates formed by copper when treated with an alkali thiocyanate and an organic base. These have the general formula $[CuB_2(CNS)_2]$, where B is pyridine[13,14,15], benzidine[16] or *o*-anisidine[17]. Nickel, cobalt, silver, iron (II) and mercurous salts interfere.

On shaking copper sulphate with an acetone solution of an alkali metal thiocyanate, a blood-red colour is formed. On dilution with water, the red colour disappears, the solution becomes olive-green, and white CuCNS deposits. It has been suggested[18] that the red colour is due to $M_2[Cu(CNS)_4]$ or $M[Cu(CNS)_3]$, and its formation has been made the basis of a suggested method of estimation[19]. The method has the disadvantages that the coloured complex is unstable, and that it is necessary to work in an anhydrous solution.

DISCUSSION

In the present work, a stable, solid compound, triphenylmethylarsonium tetrathiocyanatocuprate(II), $[Ph_3MeAs]_2[Cu(CNS)_4]$, has been isolated. The compound, which is formed by the addition of triphenylmethylarsonium chloride and ammonium thiocyanate solutions to an acid solution of the copper (II) ion, can be extracted from the aqueous reaction mixture with *o*-dichlorbenzene, and the resultant red-brown solution is stable and suitable for the colorimetric micro-estimation of copper. This solution has a broader absorption curve than the corresponding iron and cobalt compounds, the absorption maximum being at 498 mμ.

The reaction constitutes a sensitive test for copper, detecting 1 μg of copper per ml, *i.e.* 1 in 1,000,000, if the resultant compound is extracted with several drops of *o*-dichlorbenzene or chloroform.

The colour of the solution was found to have a stability closely comparable to that of the iron compound, since it faded by 1% in 3 hours, and about 3% in 24 hours. This represents a very great increase over the stability of cupric thiocyanate or the metallic thiocyanatocuprates.

In the formation of the copper complex it was found important that the triphenylmethylarsonium chloride be added before the ammonium thiocyanate. If they were added in the reverse order, appreciable reduction to cuprous thiocyanate resulted and a low reading was obtained.

Since an extraction technique was used, the depth of colour was virtually independent of the amount of NH_4CNS added, provided the aqueous layer was saturated with $Ph_3MeAsCNS$.

Pure triphenylmethylarsonium tetrathiocyanatocuprate (II), when in solution in *o*-dichlorbenzene or chloroform, appeared to dissociate with the elimination of a molecule of triphenylmethylarsonium thiocyanate. A similar behaviour was shown by solutions of triphenylmethylarsonium hexathiocyanatoferrate (III)[20]. The dissociation, which was accompanied by a shift of the absorption maximum from 498 mμ to 492 mμ was probably due to the equilibrium:

$$[Ph_3MeAs]_2[Cu(CNS)_4] \rightleftarrows Ph_3MeAsCNS + [Ph_3MeAs][Cu(CNS)_3].$$

During the estimation of copper, a large excess of triphenylmethylarsonium thiocyanate is present in the solution, and hence the equilibrium is moved almost entirely to the left.

The thiocyanate groups appeared to be only loosely attached to the copper, and could be replaced partially by chloride ion. As a result, the depth of colour of the *o*-dichlorbenzene solution was appreciably reduced by the addition of large quantities of triphenylmethylarsonium chloride. The effect is illustrated in Table I. It will be noted that triphenylmethylarsonium perchlorate has a negligible effect.

In an actual copper estimation, any chloride ions in the aqueous phase appear to pass into the *o*-dichlorbenzene chiefly as hydrochloric acid, since triphenylmethylarsonium thiocyanate has a very low water-solubility compared to triphenylmethylarsonium chloride. The difficulty can thus be overcome simply by buffering the aqueous phase with sodium acetate.

TABLE I

EFFECT OF ARSONIUM SALTS ON SOLUTION
$[Ph_3MeAs]_2[Cu(CNS)_4]$. (40 μg of Cu per ml).

Solution	Arsonium salt added	Depth of colour in terms of Solution (a).
(a)	Nil	1.00
(b)	5 equivalents $Ph_3MeAsCNS$	1.42
(c)	5 equivalents $Ph_3MeAsCl$	0.71
(d)	(5 equivalents $Ph_3MeAsCNS$) (+ 5 equivalents $Ph_3MeAsCl$)	1.11
(e)	5 equivalents $Ph_3MeAsClO_4$	0.96

The method is capable of determining from 10 to 100 μg of copper per ml with an accuracy of ± 2%, except at the extreme lower end of the range, where the percentage variation is somewhat higher. This accuracy can be maintained in the presence of large quantities of nickel, aluminium and manganese without modification or separation, and after suitable modification, but without separation, in the presence of large amounts of molybdenum, cadmium and zinc. Chromium and iron will give satisfactory results with simple partial separation. Cobalt alone interferes strongly and should be absent. Test solutions within the pH range of 1 and 5 are satisfactory, except in the presence of large concentrations of chloride or nitrate, when the solution should be buffered with sodium acetate.

The solutions obey Beer's law over most of the suggested concentration range, deviating slightly close to the upper limit.

EXPERIMENTAL

Triphenylmethylarsonium tetrathiocyanato cuprate (II)

$[Ph_3MeAs]_2[Cu(CNS)_4]$. To a solution of triphenylmethylarsonium chloride (2%, 125 ml) was added ammonium thiocyanate (10 g) in concentrated filtered solution, together with enough water to keep the solution clear (700 ml). This was cooled in ice, and to it was added with stirring a faintly acid solution of A.R. $CuSO_4.5H_2O$(0.74 g). The complex arsonium thiocynatocuprate separated as a fine brown suspension which coagulated on stirring, after filtration with a sintered glass funnel, the precipitate was washed thoroughly with distilled water and dried in a vacuum desiccator. On standing at room temperature, the compound sintered slightly. It was soluble in acetone, chloroform, ethylene dichloride and *o*-dichlorbenzene, and insoluble in water, benzene, petroleum ether and carbon tetrachloride.

Calculated for $[Ph_3MeAs]_2[Cu(CNS)_4]$; C = 53.75%; H = 3.87%; N = 5.97%; Cu = 6.77%; As = 15.97%
Found: C = 54.03%; H = 4.10%; N = 6.06%; Cu = 6.82%; 6.79%; As = 15.73%, 15.95%.

PROCEDURE

In a small separating funnel put *o*-dichlorbenzene (b.p. 180° to 183° C) (5 ml), then pipette in 10 ml of copper solution, which should contain between 10 and 100 μg of copper per ml and have a pH of 1 to 5. If appreciable amounts of nitrate or chloride are present, add 1 ml of *N* sodium acetate. To this add 2 ml of 1% triphenylmethylarsonium chloride, then 1 ml of 25% ammonium thiocyanate solution (previously treated with a few drops of $Ph_3MeAsCl$ solution, and extracted with *o*-dichlorbenzene to remove traces of iron). Shake out arsonium thiocyanatocuprate (II) with *o*-dichlorbenzene and filter through a No. 2 sintered-glass filter. Extract the aqueous layer with a further 1 ml of *o*-dichlorbenzene. To the aqueous layer add 1 ml of 1% triphenylmethylarsonium chloride solution and extract twice with *o*-dichlorbenzene. Repeat this once more, then wash combined filtered extracts into a 25 ml graduated flask, make up to the mark, and compare with a blank solution in a "Spekker" photoabsorptiometer, using 0.5 cm cells, heat absorption filters H503 and blue-green spectrum filters 603. Obtain copper content of solution by reference to a calibration curve prepared by treating a series of known solutions of copper in the same manner as above.

RESULTS

Results obtained over the whole range suggested are shown in Table II. The average mean deviation is usually about 1%, and only barely exceeds 2% at the lower end of the range.

TABLE II

SAMPLES (10 ml) CONTAINING 10 TO 100 μg OF COPPER PER ml

Cu used (μg/ml)	Cu found Min.	(μg/ml) Max.	Mean Deviation (μg/ml)	Mean Deviation (%)
10	9.75	10.25	0.25	2.5
20	20.0	20.0	0.00	0.0
30	30.0	30.0	0.00	0.0
40	39.5	41.0	0.75	1.9
50	49.5	50.5	0.50	1.0
60	59.5	60.5	0.50	0.8
70	69.5	71.0	0.75	1.1
80	79.0	80.5	0.75	0.9
90	89.5	91.0	0.75	0.8
100	99.0	101.0	1.00	1.0

INTERFERENCE

Anions. If sulphuric acid only was present, the pH could be as low as 1, but in the presence of appreciable quantities of chloride and nitrate, the pH could not be below 3. Buffering with sodium acetate gave a satisfactory result. Reducing agents should be absent. Acetate and fluoride could be tolerated in fairly high concentration, but the tolerance to phosphate was relatively low. These results are shown in Table III.

TABLE III

SAMPLES (10 ml) CONTAINING 100 μg OF COPPER PER ml

Substance added	Concentration	Cu found (μg/ml)	Error %
H_2SO_4	*N*	102.5	+2.5
	N/10	100.0	0.0
HCl	*N*/1,000	98.0	—2.0
	N/100 + *N*/10 NaAc	98.0	—2.0
	N/10 + *N*/5 NaAc	98.0	—2.0
HNO_3	*N*/1,000	98.0	—2.0
	N/100 + *N*/10 NaAc	98.0	—2.0
	N/10 + *N*/5 NaAc	98.0	—2.0
NaAc	*N*/3	98.0	—2.0
NH_4Cl	2*N*	99.4	—0.6
NH_4NO_3	2*N*	99.4	—0.6
$(NH_4)_2SO_4$	2*N*	98.0	—2.0
NaF	1/10th saturated	98.0	—2.0
Na_2HPO_4	*N*/30	98.0	—2.0
$Na_2S_2O_3$	*N*/500	99.0	—1.0

Cations. The interference caused by the presence of other cations was determined by introducing them into a standard solution of copper containing 100 μg per ml. The results are shown in Table IV for concentrations causing a variation of 2% of the copper estimated.

TABLE IV

Metal	Interfering concn.(μg/ml)	Reading too high (+) or too low (—)	X Cu concn.
Co	5	+	0.05
Cr	1,000	—	10
Mn	10,000	Nil	100
Ni	10,000	—	100
Al	10,000	—	100
Cd (i)	10,000	—	100
Zn (ii)	1,000	+	10
Fe (III)	1	+	0.01
Fe (III) + ml sat. NaF	100	—	1.0
Mo (V)	5		0.05

(i) A total of 8 ml of 10% $Ph_3MeAsCl$ used.
(ii) A total of 20 ml of 1% $Ph_3MeAsCl$ and 2 ml of 25% NH_4CNS used.

The tolerance to nickel, manganese, aluminium and cadmium was very high, while the interference by chromium and iron was such that simple partial separations would be enough to give a satisfactory result. Interference by Mo (V) sould be eliminated by oxidation to Mo (VI). Cobalt only interfered strongly and chould be absent.

SUMMARY

Triphenylmethylarsonium thiocyanate is recommended for the colorimetric micro-estimation of copper. The procedure is suitable within a range of 10 to 100 µg of copper per ml with an accuracy of about 2%. It enables the micro-estimation of copper to be carried out on most of its common alloys without prior separation. A stable copper complex of the type $[R_4As]_2[Cu(CNS)_4]$ has been isolated.

RÉSUMÉ

Le thiocyanate de triphénylméthylarsonium est recommandé pour le microdosage colorimétrique du cuivre. Ce procédé permet de doser des teneurs de 10 à 100 µg de cuivre par ml, avec une précision d'environ 2%. On peut ainsi effectuer des microdosages de cuivre dans la plupart de ses alliages courants, sans séparation préalable. Un complexe stable, du type $[R_4As]_2[Cu(CNS)_4]$, a été isolé.

ZUSAMMENFASSUNG

Triphenylmethylarsoniumthiocyanat wird zur kolorimetrischen Mikrobestimmung von Kupfer empfohlen. Das Verfahren ist in einem Bereich von 10-100 µg Kupfer pro ml mit einer Genauigkeit von ungefähr 2% anwendbar. Es ermöglich die Mikrobestimmung des Kupfers ohne vorherige Abtrennung in den meisten seiner gebräuchlichen Legierungen. Ein stabiler Cu-Komplex des Type $[R_4As]_2[Cu(CNS)_4]$ wurde isoliert.

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DIRECT HETEROMETRIC MICROTITRATION OF NICKEL WITH DIMETHYLGLYOXIME IN THE PRESENCE OF OTHER METALS

by

M. BOBTELSKY AND Y. WELWART

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem (Israël)

INTRODUCTION

This investigation is a continuation of our study on nickel dimethylglyoxime. It is our intention to present a general study of the conditions necessary for the heterometric determination of micro quantities of nickel in the presence of large excesses of other metals.

In the presence of metal complex binders and foreign metals, the maximum optical density value is generally reduced and the initial precipitation occurs late. A somewhat higher nickel concentration (0.88 mg) than usual was therefore used. But as the results show, a lower concentration of nickel may suffice for the determination. In most of the analysed solutions, the foreign metal amounted to ∾ 98%. To retain the latter in solution we tried three different metal complex binders (citrate, tartrate and tripolyphosphate). In addition, a solution of sodium acetate, in the absence of binders, was used. This study is of a general character and further investigation in special cases is required.

TECHNIQUE

The same apparatus and the same technique were used as in the previous investigation[1]. The reaction cylinder had a diameter of ∾ 3.8 cm. The vertical solution layer was therefore about 2 cm. A red filter was used in all titrations. No other filters were required even if the solution was intensively coloured by the foreign metal. (It was assumed that the foreign metal salt does not participate at all in the reaction.) A microburette (0.01 ml) was used. The first maximum density point was obtained from enlarged curves either by determining the point of intersection of the density curve with the horizontal line drawn through the maxima points, or by determining the first contact point of the density curve with the horizontal line.

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REAGENTS

The reagents were either analytical reagents or chemically pure.

RESULTS

All the results obtained are compiled in four tables. The course of titration for some cases is given in Figs. 1 and 2. The same numbers were used in the tables and in the figures.

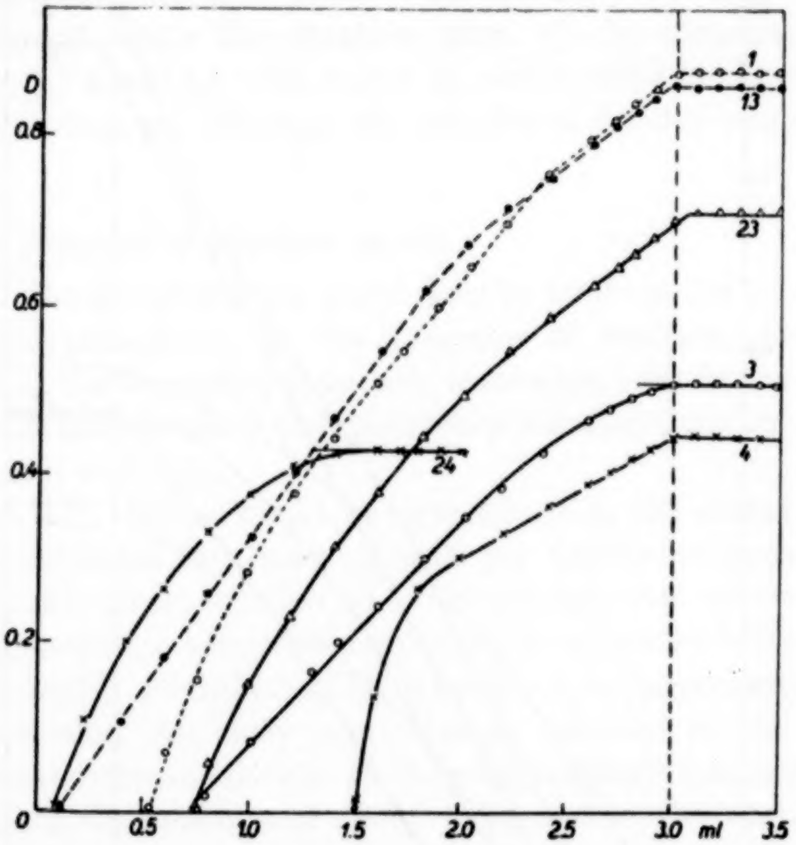

Fig. 1. Titration curves of nickel with dimethylglyoxime.

Influence of supplements

Citrate and tartrate solutions. (Tables II and III, Fig. 1). These metal binders were used separately in the absence of ammonia, but no precipitation of nickel with dimethylglyoxime occurred. The binders were used, therefore, in the presence of ammonia only. From the results obtained we learn that either binder may be used under appropriate conditions. In some cases the behaviour of the metal-binders was different and only one of them could be used. Chromium gives a precipitate with tartrate even before the addition of dimethylglyoxime, while in the presence of citrate no precipitation occurred at all. In the presence of copper or cobalt no precipitation occurred with dimethylglyoxime. But in the presence of smaller quantities of cobalt (exp. 36) the determination of nickel could be made, although the initial precipitation occurred late. In the presence of manganese, only a tartrate solution could be used. It is very remarkable that in the presence of citrate the maximum density point was obtained at *half* the calculated amount of dimethylglyoxime, *i.e.* at 1 Ni:1 Dimethyl. This strange behaviour requires a further study. In the presence of magnesium, only a citrate solution could be used as the tartrate gave a precipitate with magnesium, even before the beginning of the titration.

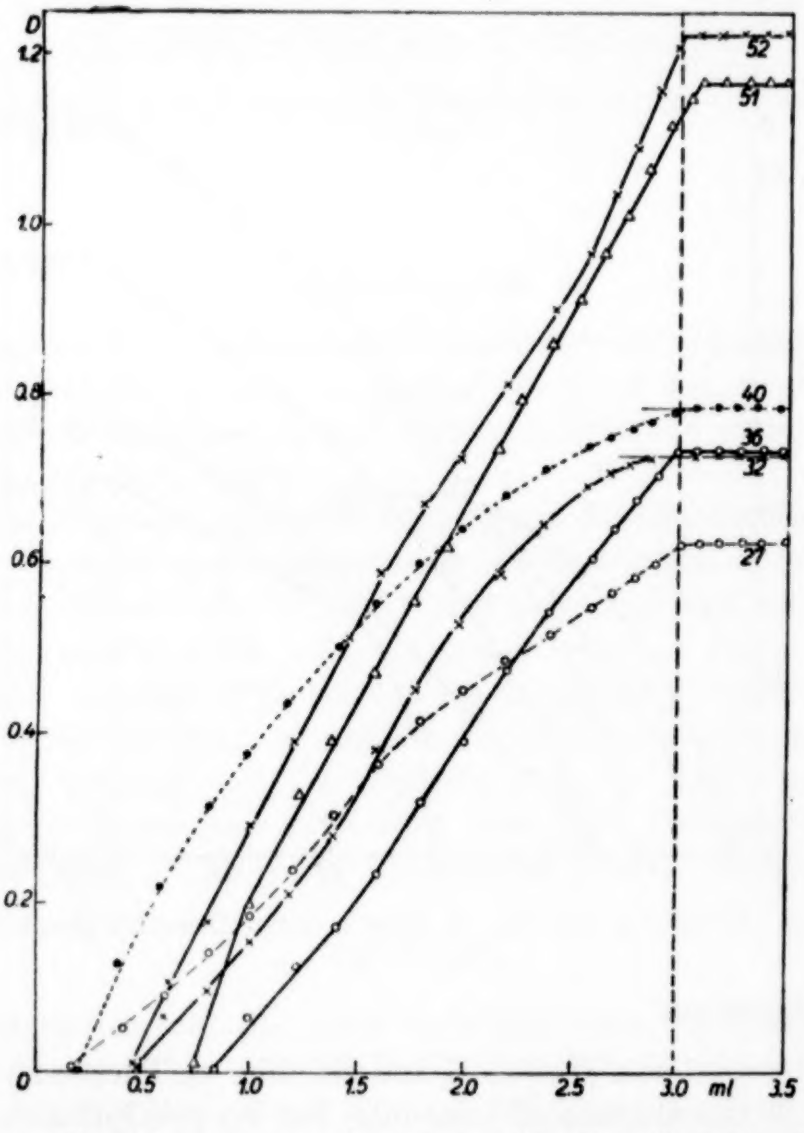

Fig. 2. Titration curves of nickel with dimethylglyoxime.

Tripolyphosphate solution. (Table IV and Fig. 2). Chromium and lead gave a precipitate just as with tartrate. High maximum density values of nickel were obtained in the presence of zinc and magnesium (exps. 51 and 52). We may, therefore, expect a much higher sensitivity in determining small quantities of nickel in the presence of these metals. In a copper solution of a lower concentration (∼ 87% copper) and in a cobalt solution (85% cobalt), nickel could be determined (exps. 47 and 49) with an error of nil to 0.3 microgram.

Sodium acetate solution. (Table I and Fig. 1). These titrations were carried out with the purpose of studying the nickel determination in the *absence* of special metal complex binders. In the presence of iron, copper or cobalt (exps. 2, 7 and 8) no precipitate with dimethylglyoxime occurred. In a more dilute cobalt solution (exp. 9), the density increased indefinitely. In the presence of cadmium, manganese, zinc or magnesium, no special metal complex binders were required at all and the determination of nickel could be made in the acetate solution. In lead solution a precipitate appeared before the titration (exp. 5). In chromium (>98%) and aluminium (∼97%) solutions (exp. 3 and 4), nickel could be determined. Theoretical results were obtained although the maximum density values were reduced in both cases.

Titration in the presence of trivalent metals

Iron (98.5%). The determination could only be made in the presence of citrate, tartrate or tripolyphosphate. In the presence of tartrate, the precipitation occurred almost at the beginning (exp. 28); somewhat later in the citrate solution (exp. 14), and still later in the tripolyphosphate solution (exp. 41). Error between nil (polyphosphate) and 3%.

Chromium (98.3%). Nickel could be determined in the acetate solution only. The precipitate appeared late (exp. 3) and the maximum density was low. The error was nil. In citrate solution no nickel precipitation occurred, while in the tartrate or polyphosphate solutions a precipitate appeared before the titration.

Aluminium (∼97%). Nickel could be determined in the presence of each of the four supplements used. An early precipitation occurred in the tartrate, and somewhat later in the citrate solution. In the polyphosphate solution the precipitate appeared only after the addition of about 30%, and in the acetate after 50%, of the dimethylglyoxime required. In both the latter cases the danger may therefore exist that in more dilute nickel solutions no precipitate with dimethylglyoxime will be obtained. In addition, in the acetate solution, the maximum density value is reduced. In the citrate and tartrate solutions the error was nil. Error between nil (acetate or citrate) and 1.3%.

Titrations in the presence of divalent metals

Lead (99.6%). The nickel determination could be carried out in the presence of citrate or tartrate only (error 2%).

Cadmium (99.2%). Each of the four supplements could be used (error 1—3%).

Copper (98.8%). No precipitation of nickel occurred in the presence of any of the supplements used in a concentrated copper solution. In a more dilute copper solution (87.8%) which contained tripolyphosphate, the determination of nickel could be carried out and the error was nil (exp. 47).

TABLE I

GENERAL COMPOSITION: 5 ml 0.003M $NiSO_4$ + 2 ml aM Salt + 8 ml 0.5M Na-acetate + 5 ml H_2O + x ml 0.01M dimethylglyoxime.
Vol.: 20 ml; filter: red; Temp.: 16.5-19.5 ° mg Ni: 0.880.

Exp. No.	Salt			% Ni	x ml found	Initial precipt. at ml	Titration time in minutes	Maxim. density value	Error		
	name	molarity	mg metal						%	γ	γ/ml
1				100	3.00	0.50	15	0.88	0.0	0.0	0.0
2	$FeCl_3$	0.5	55.8	1.5		>3.50	∼(50)				
3	$Cr(NO_3)_2$	0.5	52.0	1.7	3.00	0.80	32	0.51	0.0	0.0	0.0
4	$AlCl_3$	0.5	27.0	3.2	3.00	1.50	21	0.45	0.0	0.0	0.0
5	$Pb(NO_3)_2$	0.5	207.2	0.42	*						
6	$Cd(NO_3)_2$	0.5	112.4	0.78	2.92	0.20	20	0.81	—2.7	—24.0	—1.2
7	$CuSO_4$	0.05	6.36	12.2		>3.50	∼(50)				
8	$Co(NO_3)_2$	0.5	58.9	1.5		>3.50	∼(50)				
9	,,	0.05	5.89	15.0	∞		25				
10	$MnCl_2$	0.5	54.9	1.6	3.10	0.30	20	0.88	+3.3	+29	+1.4
11	$Zn(NO_3)_2$	0.5	65.4	1.3	2.94	0.10	17	0.87	—2.0	—17.6	—0.9
12	$MgCl_2$	0.5	24.3	3.5	3.0	0.20	17	0.87	0.0	0.0	0.0

*: precipitation at beginning.
∞: density increases indefinitely.

TABLE II

GENERAL COMPOSITION: 5 ml 0.003M $NiSO_4$ + 2 ml aM Salt + 2 ml 1.0M Na_3-citrate + 4 ml 1.0M NH_3 + 2 ml 1.0M NH_4NO_3 + 5 ml H_2O + x ml 0.01M dimethylglyoxime.
Vol.: 20 ml; filter: red; Temp.: 16.5-19.5° mg Ni: 0.880.

Exp. No.	Salt			% Ni	x ml found	Initial precipt. at ml	Titration time in minutes	Maxim. density value	Error		
	name	molarity	mg metal						%	γ	γ/ml
13				100	2.98	0.10	15	0.87	—0.7	—6.0	0.3
14	$FeCl_3$	0.5	55.8	1.5	2.90	0.40	24	0.70	—3.2	—29	—1.4
15	$Cr(NO_3)_3$	0.5	52.0	1.7		>3.50					
16	$Cr(NO_3)_3$	[1] 0.5	52.0	1.7		>3.50	18				
17	$AlCl_3$	0.5	27	3.2	3.00	0.30	17	0.79	0.0	0.0	0.0
18	$Pb(NO_3)_2$	0.5	207.2	0.42	2.94	0.10	12	0.80	—2.0	—17.6	—0.9
19	$Cd(NO_3)_2$	0.5	112.4	0.78	2.96	0.40	13	0.85	—1.3	—11.4	—0.6
20	$CuSO_4$	0.5	63.5	1.2		>3.50	(28)				
21	$CuSO_4$	0.05	6.35	12.2		>3.50					
22	$Co(NO_3)_2$	0.5	58.9	1.5		>3.50	~(52)				
23	$Co(NO_3)_2$	0.05	5.89	15	3.04	0.80	18	0.71	+1.3	+11.4	+0.6
24	$MnCl_2$	0.5	54.9	1.6	1.5	0.10	13	0.50	0.0	0.0	0.0
25	$Zn(NO_3)_2$	0.5	65.4	1.3	2.96	0.10	18	0.75	—1.3	—11.4	—0.6
26	$MgCl_2$	0.5	24.3	3.5	2.90	0.10	21	0.85	—3.2	—29	—1.4

[1] in absence of NH_3.

TABLE III

GENERAL COMPOSITION: 5 ml $0.003M$ $NiSO_4$ + 2 ml aM Salt + 2 ml $1.0M$ K_2-tartrate + 4 ml $1.0M$ NH_3 + 2 ml $1.0M$ NH_4NO_3 + 5 ml H_2O + x ml $0.01M$ dimethylglyoxime
Vol : 20 ml; filter: red; Temp.: 16.5-19.5° mg Ni: 0.880.

Exp. No.	Salt			% Ni	x ml found	Initial precipt. at ml	Titration time in minutes	Maxim. density value	Error		
	name	molarity	mg metal						%	γ	γ/ml
27				100	3.02	0.20	10	0.64	+0.6	+5.3	+0.3
28	$FeCl_3$	0.5	55.8	1.5	2.94	0.20	14	0.85	—2.0	—17.6	—0.9
29	$Cr(NO_3)_3$	0.5	52.0	1.7	*						
30	$Cr(NO_3)_3$	0.05	5.2	16.7	*						
31	$AlCl_3$	0.5	27	3.2	2.96	0.20	20	0.69	—1.3	—11.4	0.6
32	$Pb(NO_3)_2$	0.5	207.2	0.42	2.94	0.40	13	0.715	—2.0	—17.6	—0.9
33	$Cd(NO_3)_2$	0.5	112.4	0.78	2.92	0.10	18	0.825	—2.6	—22.9	—1.1
34	$CuSO_4$	0.5	63.5	1.2		>3.50	∼(50)				
35	$Co(NO_3)_2$	0.5	58.9	1.5		>3.50	∼(50)				
36	$Co(NO_3)_2$	0.05	5.89	15.0	3.00	0.80	17	0.73	0.0	0.0	0.0
37	$MnCl_2$	0.5	54.9	1.6	2.90	0.10	17	0.92	—3.3	—29	—1.4
38	$Zn(NO_3)_2$	0.5	65.4	1.3	3.00	0.10	20	0.91	0.0	0.0	0.0
39	$MgCl_2$	0.5	24.3	3.5	*						

*: precipitation at beginning.

TABLE IV

GENERAL COMPOSITION: 5 ml 0.003*M* $NiSO_4$ + 2 ml *aM* Salt + 8 ml 0.25*M* $Na_5P_3O_{10}$ + 5 ml H_2O + *x* ml 0.01 *M* dimethylglyoxime.
Vol.: 20 ml; filter: red; Temp.: 16.5°-19.5° mg Ni: 0.880.

Exp. No.	Salt			% Ni	*x* ml found	Initial precipt. at ml	Titration time in minutes	Maxim. density value	Error		
	name	molarity	mg metal						%	γ	γ/ml
40				100	2.95	0.20	20	0.78	—1.6	—19.1	—0.7
41	$FeCl_3$	0.5	55.8	1.5	3.00	0.70	23	0.62	0.0	0.0	0.0
42	$Cr(NO_3)_3$	0.5	52.0	1.7	*						
43	$AlCl_3$	0.5	26.9	3.2	2.96	0.90	42	0.74	—1.3	—11.4	—0.6
44	$Pb(NO_3)_2$	0.5	207.2	0.42	*						
45	$Cd(NO_3)_2$	0.5	112.4	0.78	2.94	0.20	18	0.88	—2.0	—17.6	—0.9
46	$CuSO_4$	0.5	63.5	1.2		>3.50	∼(50)				
47	$CuSO_4$	0.05	6.35	12.2	3.00	0.40	29	0.78	0.0	0.0	0.0
48	$Co(NO_3)_2$	0.5	58.9	1.5		>3.50	10				
49	$Co(NO_3)_2$	0.05	5.89	15.0	2.98	0.20	16	0.64	—0.6	—5.3	—0.3
50	$MnCl_2$	0.5	54.9	1.6	3.10	0.40	12	1.0	+3.3	+29	+1.4
51	$Zn(NO_3)_2$	0.5	65.4	1.3	2.92	0.70	19	1.16	—2.6	—22.8	—1.1
52	$MgCl_2$	0.5	24.3	3.5	3.02	0.40	14	1.22	+0.6	+5.3	+0.26

*: precipitation at beginning.

Cobalt (98.5%). No precipitation of nickel occurred in the presence of any of the supplements used. In a more dilute cobalt solution (85%), nickel could be determined in the presence of each of the metal complex binders. The error was 0—1%.

Manganese (98.4%). Nickel could be determined in all cases (error 3%). In the presence of citrate (exp. 24) only *half* of the calculated dimethylglyoxime (for a complete precipitation) was required. The maximum value obtained was low.

Zinc (98.7%). Each of the four supplements could be used. In the presence of tripolyphosphate the precipitation began somewhat late (exp. 51). The error was between nil (tartrate) and 2.6% (tripolyphosphate).

Magnesium (96.5%). In the presence of tartrate a precipitate appeared before the titration. The determination could be carried out in the presence of all other supplements. Error was between nil (acetate) and 3.2% (citrate).

METHOD

General procedure. 20 ml of the analysed solution are titrated with a 0.01*M* dimethylglyoxime which is added drop by drop from a microburette (0.01 ml). The solution is stirred continuously and the readings on the galvanometer are made only when they become constant, which takes from a few seconds to a minute. (The light passes vertically through a layer of about 2 cm.) A red filter is used.

Composition. The following four solutions are used. The choice of the specific solution depends on the foreign metal (∿98%) present.

1. *Citrate solution.*	To 15 ml of the analysed solution are added: 2 ml 1.0*M* Na_3 citrate + 2 ml 2.0*M* NH_3 + 1 ml 2.0*M* NH_4NO_3.
2. *Tartrate solution.*	To 15 ml of the analysed solution are added: 2 ml 1.0*M* Na_2 (K_2)-tartrate + 2 ml 2.0*M* NH_3 + 1 ml 2.0*M* NH_4NO_3.
3. *Na- acetate solution.*	To 20 ml of the analysed solution is added 1 ml 4.0*M* Na-acetate.
4. $Na_5P_3O_{10}$ *solution.*	To 12 ml of the analysed solution are added: 8 ml 0.25*M* $Na_3P_3O_{10}$.

Determination of nickel

In aluminium.	All four solutions may be used alike.
In iron (III).	Citrate, tartrate or phosphate solutions may be used.
In chromium.	Only acetate solution may be used.
In lead.	Citrate or tartrate solutions may be used.
In cadmium.	All four solutions may be used.
In copper (∿ 87.5).	Phosphate may be used.
In cobalt (∿ 85.0).	Citrate, tartrate or phosphate may be used.
In manganese.	Tartrate, phosphate or acetate may be used.
In zinc.	All solutions may be used.
In magnesium.	Citrate, phosphate or acetate may be used.

In the presence of mixtures of metals the solution selected must be suitable for the determination of nickel in each of the foreign metals. For example: in a mixture of aluminium and iron, citrate, tartrate or phosphate solutions may be used; in a mixture of chromium and aluminium, only an acetate solution can be used.

SUMMARY

A new "heterometric" method was presented for a quick, direct determination of small quantities (< 1 mg) of nickel (∼ 2%) in the presence of other metals (∼ 98%). The error was between zero and 1.4 micrograms of nickel per ml, or between zero and 3% of nickel.

RÉSUMÉ

Une nouvelle méthode ,,hétérométrique" est présentée pour la détermination rapide de petites quantités (< 1 mg) de nickel (∼ 2%) en présence d'autres métaux (∼ 98%). L'erreur est comprise entre 0 et 1.4 micrograms (ou de 0 à 3% de nickel).

ZUSAMMENFASSUNG

Eine neue ,,heterometrische" Methode zur raschen direkten Bestimmung von Kleinen Mengen (< 1 mg) Nickel (∼2%) in Gegenwart von anderen Metallen (∼ 98%) wird presentiert. Der Fehler liegt zwischen null und 1.4 Mikrogramm oder zwischen null und 3% Nickel.

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POTENTIOMETRIC DETERMINATION OF TITANIUM WITH VANADIUM

by

M. C. STEELE AND F. M. HALL

Chemistry and Metallurgy Department, Technical College, Wollongong (Australia)

Titanium is a metal of atomic weight 47.90 which is classified in group IVB of the Periodic Table. Being transitional it has variable valencies forming di-, tri-, and tetra-valent compounds[1].

Vanadium is a metal of atomic weight 50.95 classified in sub group V of the Periodic Table. It also has variable valencies forming di-, tri-, tetra- and penta-valent compounds.

Organic compounds which have been reported as giving a colour with titanium have an ene-diol group and at least one hydroxy group:

Chromotropic acid, 1,8 naphthol 3,6 disulphonic acid[9,10]; disodium 1,2 dihydroxybenzene 3,5 disulphonate[11]; salicylic acid[12]; gallic acid[9]; thymol[13,14]; dihydroxymaleic acid; catechol; ascorbic acid[15].

Precipitants such as cupferron, 8-hydroxyquinoline[8], *p*-hydroxyphenol arsonic acid have been used for gravimetric determination and/or for the isolation of titanium from interfering elements.

VINOHUROV[16] has reported a method for the spectral analysis of non-rusting steels for titanium in the ultraviolet region.

The development of pertitanic acid with hydrogen peroxide and its subsequent determination colorimetrically is a well-established method for titanium.

TSUGUO SAWAYA AND MASAO YAMASHITA[17] have determined titanium by neutralising its solution with potassium hydroxide using bromocresol purple as indicator and adding to an excess of potassium fluoride solution and 0.1*N* hydrochloric acid; the excess hydrochloric acid being titrated with potassium hydroxide. This method would not be suitable for small amounts of titanium such as in steels.

This paper gives consideration to the potentiometric determination of titanium particularly in steel, and the estimation of vanadium in the same sample, if present.

Due to its reduction by zinc metal and amalgams to the trivalent state and the subsequent stoichiometric re-oxidation by, for example, permanganate, such a method can be employed for volumetric determinations of titanium. Zinc, however, reduces many metals so the interfering elements should be removed prior to reduction.

The mercury cathode method of electrolytic deposition[2,3,4,5] will remove most metals; of these metals which might be expected to be present in ferrous metals only titanium, vanadium and molybdenum are left in the solution after mercury cathode methods of removal. Molybdenum, if present, can be removed by acid sulphide precipitation, leaving then only titanium and vanadium in the solution which would be capable of reduction.

The subsequent determinations may now be effected by reduction and re-oxidation methods, employing potentiometric or volumetric methods.

Both titanium and vanadium can be readily reduced and re-oxidised. Sulphur dioxide has no effect on Ti^{+4} and reduces V^{+5} to V^{+4}. Being stable to atmosphere V^{+4} may then be re-oxidised by permanganate. This re-oxidation should be done hot as the reaction is slow in the cold. Zinc, however, is a far more powerful reducing agent than sulphur dioxide and reduces Ti^{+4} to Ti^{+3} and V^{+5} through V^{+4} and V^{+3} to V^{+2}. The re-oxidation of Ti^{+3} to Ti^{+4} and V^{+2} to V^{+4} occurs rapidly in air hence a carbon dioxide atmosphere is necessary to avoid this re-oxidation.

Table I shows the oxidation-reduction potentials of the ions concerned in the subsequent procedures.

TABLE I

Oxidised form	Reduced form	Electrode reaction	Eo (Volts)
MnO_4^-	Mn^{+2}	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{+2} + 4H_2O$	+1.50 (H = 1)
VO_4^{-3}	VO^{+2}	$VO_4^{-3} + 6H^+ + e \rightleftharpoons VO^{+2} + 3H_2O$	+1.2 (H = 1)
Fe^{+3}	Fe^{+2}	$Fe^{+3} + e \rightleftharpoons Fe^{+2}$	+0.76
VO^{+2}	V^{+3}	$VO^{+2} + 2H^+ + e \rightleftharpoons V^{+3} + H_2O$	+0.4 (H = 1)
Ti^{+4}	Ti^{+3}	$Ti^{+4} + e \rightleftharpoons Ti^{+3}$	—0.04
V^{+3}	V^{+2}	$V^{+3} + e \rightleftharpoons V^{+2}$	—0.2

Owing to these redox potentials, Ti^{+3} reduces Fe^{+3} to Fe^{+2}, V^{+2} reduces Fe^{+3} to Fe^{+2}, V^{+3} also reduces Fe^{+3} to Fe^{+2}, but V^{+4} has no effect on Fe^{+3}, a stronger oxidising agent being required to give V^{+5}. Hence if Ti^{+3} and V^{+2} are added to Fe^{+3} solution the amount of Fe^{+2} formed is equivalent to all the titanium and two thirds of the vanadium, the other one third of vanadium requires a stronger oxidising agent such as permanganate.

It was found that reduction with a Jones' reductor[6] gave inconsistent and incomplete reduction; a far more satisfactory method being to boil the solution with zinc metal for approximately thirty minutes. To prevent re-oxidation due to atmosphere the whole should then be cooled under carbon dioxide, preferably

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employing ice, and the solution rapidly decanted from the zinc into an excess of acid ferric alum solution. The solution now consists of Fe^{+3}, Fe^{+2} (equivalent to Ti and 2/3V) and V^{+4} and may be potentiometrically titrated in the hot with standard permanganate. To ensure a sharp rise in E.M.F. at the completion of the ferrous oxidation, phosphoric acid is added before the titration is commenced. The effect is in lowering the redox potential of the Fe^{+3}/Fe^{+2} system by complexing the Fe^{+3}, and the amount required is just in excess of that necessary to remove the ferric colour from the solution.

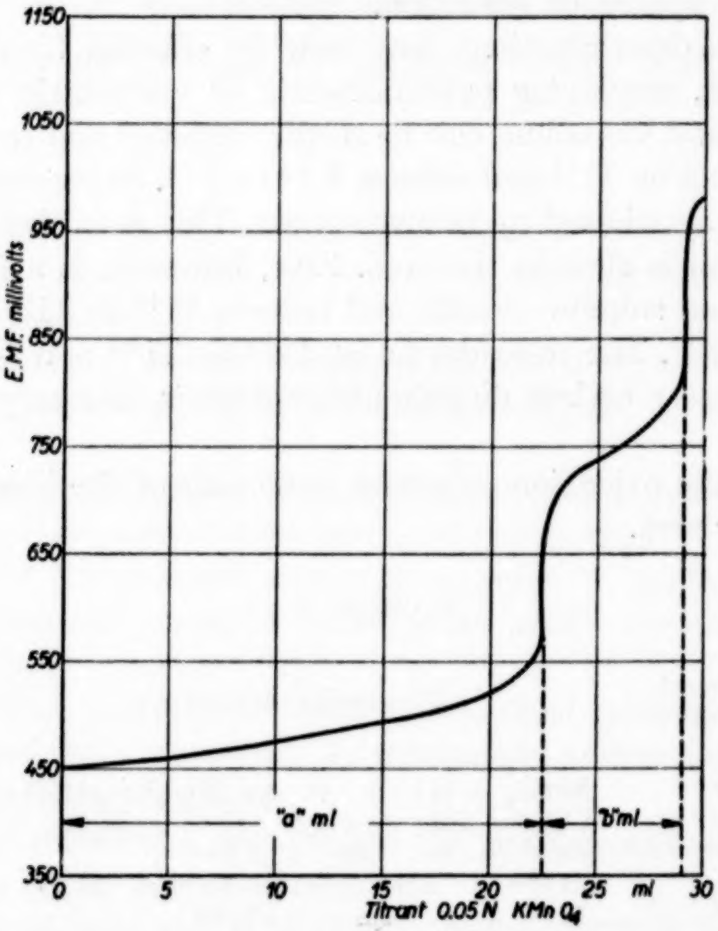

Fig. 1.

Fig. 1 shows a typical graph of this titration employing platinum-calomel electrodes. If $0.05N$ $KMnO_4$ is the oxidant then *b* ml are required to oxidise V^{+4} to V^{+5}, 1 ml $0.05N$ $KMnO_4$ = 0.002547 g V, and (*a*-2*b*) ml required to oxidise Ti^{+3} to Ti^{+4}, 1 ml $0.05N$ $KMnO_4$ = 0.002395 g Ti.

The potentiometric titration apparatus can be of any type but preferably with means for agitation[7].

As an alternative to this potentiometric method the determination can be effected by reducing the solution, after the mercury cathode deposition, with sulphur dioxide, boiling briskly to clear of SO_2 (SO_2 reduces $KMnO_4$) and titrating the V^{+4} so formed to V^{+5} with $0.05N$ $KMnO_4$. This solution is then reduced with zinc metal as before, cooled under CO_2, added to excess ferric solution and titrated hot with permanganate.

Titration with $KMnO_4$ after SO_2 reduction is equivalent to *b* ml in Fig. 1 whilst the total titration after the zinc reduction is to the permanent pink of permanganate and equivalent to $(a+b)$ ml in Fig. 1.

The percentage of both the titanium and vanadium can then be calculated. For example — on a 2 gram sample

$$\%V = \text{gram equivalents of V per ml of titrant} \times b \text{ ml of titrant} \times \frac{100}{2}$$

$$= 0.002547 \times (29.1 - 22.4) \times \frac{100}{2}$$

$$= 0.853\%.$$

$$\%Ti = \text{gram equivalents Ti per ml of titrant} \times (a - 2b) \text{ ml} \times \frac{100}{2}$$

$$= 0.002395 \times (22.4 - 13.4) \times \frac{100}{2}$$

$$= 1.08\%$$

METHOD

Dissolve up to 2 grams of the steel in 1:1 H_2SO_4. If other acids are necessary for solution then after solution fume to SO_3. Dilute with water to not more than 100 ml and adjust acidity, with NH_4OH, to a minimum without precipitation. Transfer the solution to a mercury cathode apparatus and apply 8-10 volts and a current density of approximately 0.3 amp/cm² [2]. Agitation of the mercury with nitrogen or mechanical stirrer is desirable. After electrolysis is complete, separate the solution from the mercury and proceed as follows:

(a) Acidify with H_2SO_4, add zinc pellets and boil gently for thirty minutes, cool with ice under CO_2 using Schiebler guards and decant the solution rapidly into excess acid ferric alum solution. Add phosphoric acid till the solution is decolourised and 10 ml in excess, heat to at least 60° C and titrate with $0.05N$ $KMnO_4$ employing a potentiometric apparatus.

(b) Acidify with H_2SO_4, warm and pass SO_2 gas. Remove excess SO_2 by boiling and titrate hot with $0.05N$ $KMnO_4$. Then reduce this solution with zinc as in (a), cool under CO_2, add to excess acid ferric alum solution and titrate hot with $0.05N$ $KMnO_4$.

1 ml $0.05N$ $KMnO_4$ = 0.002547 g V ($V^{+4} \rightarrow V^{+5}$)
1 ml $0.05N$ $KMnO_4$ = 0.002395 g Ti($Ti^{+3} \rightarrow Ti^{+4}$)

SUMMARY

Titanium and vanadium may be determined in the same sample by removing the interfering elements, such as iron, by the mercury cathode method of deposition, reducing the titanium and vanadium with zinc, adding to a ferric solution and titrating potentiometrically with permanganate.

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RÉSUMÉ

On peut déterminer le titane et le vanadium dans un même échantillon en éliminant les éléments gênants, tels que le fer ,par électrolyse sur une cathode de mercure. Le titane et le vanadium sont réduits par le zinc; on ajoute une solution ferrique et on titre par le permanganate, au moyen d'un potentiomètre.

ZUSAMMENFASSUNG

Titanium und Vanadium können in ein und demselben Versuch bestimmt werden wenn vorher alle anderen Elemente, wie z.B. Eisen, mittels der Quecksilber-Kathoden-Methode ausgeschieden werden. Titanium und Vanadium werden dann mit Zink reduziert, zu einer eisenhaltigen Lösung hinzugefügt, und mit Permanganat potentiell titriert.

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REVUE DE LIVRES

Proceedings of the International Congress on Analytical Chemistry, Oxford, England, septembre 1952. Editeurs: W. Heffer & Sons Ltd., Cambridge, England. 493 pages. Prix: 42*s*.

Cet ouvrage publie les actes du Congrès International de Chimie Analytique qui s'est tenu à Oxford du 4 au 9 septembre 1952, sous le patronage de l'Union Internationale de Chimie Pure et Appliquée, sous la présidence de Sir ROBERT ROBINSON.

Ce livre, fort bien présenté, nous donne un exposé des travaux des différentes Sections:

Section	I:	Méthodes microchimiques
,,	II:	Méthodes biologiques
,,	III:	Méthodes électriques
,,	IV:	Méthodes optiques
,,	V:	Méthodes radiochimiques
,,	VI:	Complexes organiques
,,	VII:	Statistiques
,,	VIII:	Méthodes chromatographiques
,,	IX:	Méthodes diverses

Il donne également la liste des membres ayant participé à ce Congrès, ainsi qu'un index par nom d'auteur et un index des sujets traités.

Nous ne pouvons que recommander à nos lecteurs cet ouvrage d'actualité, se rapportant à tous les domaines de la Chimie Analytique.

P. E. WENGER (Genève)

Chimie Générale. Application de la théorie des ions. Systèmes dispersés par PAUL PASCAL, Masson & Cie, Paris, 1952. 1 Volume de 386 pages, 119 figures. Prix: 2200 fr. français.

Ce quatrième volume cloture le traité de chimie générale dû au même auteur L'ensemble constitue un travail de grande portée pour l'enseignement des bases théoriques de la chimie. Aucun chimiste ne pourrait l'ignorer.

Après l'atomistique et les problèmes fondamentaux de structure (1949), la cinétique, thermodynamique et les équilibres (1950), l'individu physico-chimique (1951), le dernier volume approfondit d'une part la notion d'acide et de base et d'autre part les systèmes dispersés.

L'auteur passe en revue les théories d'Arrhenius, puis de Brönsted et enfin celle de Lewis et expose les applications des notions acide et base à l'analyse: pH et sa mesure et courbes de neutralisation, indicateurs, erreurs, etc. L'oxydoréduction n'est cependant pas traitée ici; il faut se reporter à ce sujet au second volume. D'ailleurs il ne s'agit pas d'un traité de chimie analytique, mais bien d'un exposé de caractère très général, occupant un peu moins de deux cents pages.

L'autre moitié du volume est consacrée aux systèmes dispersés: dispersions dans les phases gazeuses; de liquides dans les liquides; dispersions mésomorphes: p.e. le système savon-eau; dispersions microcristallines dans les liquides et dans les solides; dispersions macromoléculaires; étude des gels et des gelées; équilibre de Donnan: potentiel de membrane et applications aux protéines. Ici encore l'exposé est tout-à-fait général et porte un caractère qui relève nettement des nécessités de l'enseignement universitaire. Il y est fait appel d'ailleurs aux diverses notions des autres volumes qui ont préparé en quelque sorte cette synthèse personnelle du chapitre appelé fort souvent: chimie des colloïdes.

L'ensemble des quatre volumes constitue une bonne documentation pour tous les étudiants des hautes écoles et une excellente base pour leurs recherches ultérieures.

J. GILLIS (Gand)

Progrès récents de la chromatographie. Deuxième Partie. *Chimie Minérale* par MICHAEL LEDERER, *Préface* de M. HAISSINSKY. Hermann & Cie Editeurs, Paris, 1952. 131 pages, 42 figures. Numéro 1181 de la Collection: *Actualités Scientifiques et Industrielles.*

La chromatographie peut se réjouir aujourd'hui d'un succès mérité. Après la monographie de E. LEDERER sur la chromatographie en chimie organique et biologique, cette deuxième partie, consacrée aux applications en chimie minérale, est appelée à intéresser les chimistes, praticiens ou chercheurs.

L'ouvrage envisage d'abord la chromatographie par adsorption sur adsorbants minéraux: Al_2O_3, gel de silice, ZnS, quartz activé et sur adsorbants organiques: oxine, diméthylglyoxime, charbon actif, etc. L'auteur reconnait que le mécanisme de ces séparations, dites d'adsorption, laisse à désirer ou est connu de manière très imparfaite.

La second partie est de loin la plus importante (plus de 40 pages) et expose la chromatographie de substances minérales sur papier. Diverses recettes inédites, dues à l'auteur, y ont été décrites. Cette partie, intitulée: chromatographie de partage, comprend: les principes, la technique, la séparation des cations et celle des anions, les méthodes quantitatives, l'électrochromatographie.

La troisième partie donne un aperçu de la chromatographie par échange d'ions: principes, séparation des métaux et d'acides, séparation d'isotopes, applications des échangeurs d'ions en chimie physique: constantes de dissociation, coefficients d'activité, radiocolloïdes, isothermes d'adsorption.

La bibliographie est complète jusqu'à fin 1951.

En langue française, le travail de MICHAEL LEDERER occupe une place de premier plan; nous le recommandons vivement aux chimistes.

J. GILLIS (Gand)

Applied Inorganic Analysis (2ème Edition) par G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMAN. John Wiley and Sons, New York, and Chapman and Hall, London, 1953. Un volume relié de 1034 pages, $ 15.00.

Cet important ouvrage constitue une refonte du traité de Hillebrand et Lundell (1929) très utilisé aux Etats Unis pour l'analyse des métaux, des silicates et des roches. Les nouveaux auteurs ont quelque peu rajeuni la partie théorique mais il n'apparaît pas que des données récentes aient pénétré dans la partie descriptive proprement dite. Celle-ci reste un livre de chevet avec détails opératoires pour le chimiste qui veut effectuer des séparations et qui dispose de grandes quantités pour faire son analyse. On peut alors se demander si ces recommandations qui étaient de mise il y a 50 ans trouvent encore leur place maintenant. Actuellement, qu'on le veuille ou non, il faut doser des traces et le traité de Sandell nous est beaucoup plus utile. On doit alors regretter qu'un livre de l'importance de celui-ci ne connaisse pas davantage les extractions, les dosages potentiométriques, polarographiques et spectrophotométriques. Il me semble aussi qu'il existe d'autres indicateurs de fin de réaction que ceux de pH. Contrairement à ce que je vois dans d'autres livres américains modernes, aucune tentative n'est faite pour éliminer de la gravimétrie l'emploi des hydroxydes et des sulfures, pour corriger les températures surannées de calcination. L'alumine est pesée après chauffage à 1400° et le pyrophosphate de magnésium à 1200° ! On conviendra pourtant que des progrès ont été réalisés de ce côté dans ces dernières années.

Quant au micro-analyste, il est complètement oublié ainsi d'ailleurs que les références aux travaux français. Les séparations indiquées ne sont pas toujours les meilleures et il y aurait beaucoup à redire dans le chapitre du titane et du zirconium.

En conclusion, il est grand dommage que le travail énorme que représente ce livre ne puisse plus nous servir autant que ses fondateurs l'eussent désiré; il nous semble qu'il aurait gagné à être adapté davantage aux nécessités de l'heure présente (par exemple: doser 1/10,000 de sodium dans de l'aluminium pur) pour qu'il mérite sa place dans les bibliothèques des chimistes du continent.

CLÉMENT DUVAL (Paris)

Chemical Analysis par HAROLD F. WALTON. Prentice Hall, New York, 1952. Volume relié de 435 pages et 85 figures.

Ce traité théorique d'analyse admirablement conçu et bien écrit, pour les élèves de licence ayant déjà reçu une certaine culture mathématique, traite des notions relatives à la précipitation et à la gravimétrie, à l'électrolyse, aux ions complexes, aux échanges d'ions, au potentiel d'oxydo-réduction, à l'analyse volumétrique et colorimétrique. Chaque chapitre se termine par de petits problèmes ou des questions de reflexion judicieuses. Les paragraphes les meilleurs me paraissent être les indicateurs, la méthode du dead stop, les dosages en haute fréquence. Le calcul n'est nulle part rébarbatif; il y a juste ce qu'il faut pour penser et conduire une recherche nouvelle. Les figures sont claires, bien dessinées; les tableaux placés en appendice paraissent fort utiles. Les étudiants américains connaissent maintenant la thermobalance et le parti qu'on peut en tirer pour l'analyse. L'étude de ce livre est à recommander à celui qui veut trouver en l'analyse autre chose que la recette détaillée du travail de routine. Je souhaite seulement de plus grands développements sur la polarographie et sur les méthodes d'extraction mais quelques pages supplémentaires me donneront satisfaction dans la toute prochaine seconde édition.

CLÉMENT DUVAL (Paris)

Séparation et identification des hydrocarbures dans les essences de pétrole, par M. A. BESTOUGEFF, préface du PR. LÉON JACQUÉ. Techniques et applications du pétrole, 11 Rue Magdebourg, Paris, 1952. 110 pages.

Dans cette brochure luxueusement présentée, l'auteur fait une revue générale des méthodes analytiques par traitement physique et chimique: colonnes, distillation azéotropique, distillation extractive, traitements à l'acide sulfurique et à l'urée, puis, les mesures d'indice de réfraction, les spectres infrarouges, ultraviolets, de diffusion, de masses, de rayons X, la polarisation magnétique. Il termine par un exemple concret d'analyse d'essence. L'ouvrage est complété par 254 références bibliographiques, une table d'auteurs, une table de corps cités et la table des matières. On ne relève que quelques fautes typographiques (pages 41, 56 et 110). De telles monographies nous sont fort utiles; il est souhaitable qu'elles nous tiennent périodiquement au courant des derniers progrès dans ce domaine si vaste.

CLÉMENT DUVAL (Paris)

Substances naturelles de synthèse (Volume VI) par A. ALLAIS, J. MATHIEU, A. PETIT, P. POIRIER ET L. VELLUZ. Masson et Cie, Paris, 1953. Broché et Relié. 2 Planches hors-texte, 156 pages.

Cette admirable collection poursuit sa voie et déjà on nous annonce le tome 7 avec l'adrénostérone, la cortisone, etc. J'ai déjà rendu compte ici même des volumes précédents. Les qualités de présentation matérielle, de clarté et d'intérêt scientifique se maintiennent. La formule est bonne et justement appréciée. Le tome présent contient la préparation minutieusement mise au point de l'acide désoxycholique, de l'acide glycocholique, de l'acide lithocholique, de l'adrénochrome, de la DL-cynurénine, de l'histamine, de l'hydroxy-17 désoxy-11 corticostérone et du DL-hydroxy-2 tryptophane. L'ouvrage est complété par les notes de laboratoire sur la cyclisation imidazolique, la séparation par échange d'ions et les échangeurs d'ions; les hors-textes renferment les microphotographies des corps préparés.

CLÉMENT DUVAL (Paris)

Qualitative Analysis and Analytical Chemical Separations par PHILIP W. WEST, MAURICE M. VICK AND ARTHUR L. LEROSEN (Baton Rouge, Louisiana). MacMillan, New York, 1953. Volume relié de 223 pages et 12 figures. \$ 3.75.

Les auteurs nous présentent — et l'intention est fort louable — un manuel d'analyse qualitative pour débutants qui permet de déceler les cations courants sans l'emploi de sulfures et d'hydrogène sulfuré. Ces cations sont séparés en groupes: chlorures, benzoates, fluorures, hydroxydes. On opère sur 2 ml de solution. Des cations communs comme le cérium, beaucoup moins rares que le cadmium, l'étain ou le bismuth sont omis, ainsi que le titane et le vanadium. On est tenté d'émettre des doutes sur la séparation par fluorures avec les alcalino-terreux mais il paraît qu'ils se centrifugent bien. Les anions sont séparés en 9 groupes en faisant usage notamment des sels de manganèse, de calcium, de baryum, de cadmium et d'argent. L'ouvrage est complété par des notions sur les complexes, le pH et l'oxydo-réduction. Il est difficile de juger ces méthodes sans les avoir pratiquées, mais elles me paraissent, à première vue, beaucoup plus longues que celles de Charlot et Mlle Bézier auxquelles il faut bien arriver lorsqu'on veut faire une analyse générale. J'ai été frappé par quelques fautes typographiques, notamment, pages 153 et 157; j'émets des doutes sur l'existence des cobaltiammines chlorées qui sont citées page 154, sur l'existence de l'ion $[Fe(NCS)]^{+2}$ comme responsable de la coloration rouge bien connue et sur la formule du précipité obtenu avec un sel de potassium et le cobaltinitrite de sodium.

CLÉMENT DUVAL (Paris)

MIDLANDS SOCIETY FOR ANALYTICAL CHEMISTRY
SYMPOSIUM ON ANALYTICAL CHEMISTRY 1954

Arrangements for the symposium on Analytical Chemistry to be held in the University of Birmingham between August 25 — September 1st, 1954 (cf. *Anal. Chim. Acta*, 8 (1953) 492) are progressing and it is now possible to make an interim announcement.

Lectures

There will be three or four plenary lectures. The other lectures will be divided into two distinct categories.

1) Original and unpublished work.
2) Authoritative survey of recent advances in specialised fields of Analytical Chemistry and industrial analysis.

These will include papers presented by a number of chemists of international repute.

Exhibition

There will be an exhibition of specialised apparatus by the trade and demonstrations of special techniques. There will also be on view a collection of rare old chemistry books which will include the JOSEPH PRIESTLEY collection.

Visits of scientific and non-scientific interest will be arranged. There will also be various social functions during the period of the symposium.

J. W. ROBINSON,
Hon. Secr.,
Post Office Engineering Dept.
Birmingham 9 (England)

ZUM NACHWEIS VON THALLIUM MIT RHODAMIN B IN DER TÜPFELANALYSE UND IN DER SPURENSUCHE

von

F. FEIGL, V. GENTIL UND D. GOLDSTEIN

Laboratorio da Produção Mineral, Ministério da Agricultura Rio de Janeiro (Brasil)

Die analytische Verwertung der Fällbarkeit von Thallium(III)chlorid und -Bromid aus saurer Lösung mit Rhodamin B, die zuerst, von EEGRIWE[1] bei der Verwendung dieses Farbstoffes zum Nachweis von Antimon und Wolfram beobachtet wurde, hat bisher wenig Beachtung gefunden. Das zeigt sich daran, dass weder der 2. Bericht der Internationalen Komission für neue Reaktionen und Reagenzien[2], noch ein vor kurzem erschienenes Sammelreferat[3] über Nachweis- und Bestimmungsmethoden für Thallium Hinweise auf eine wichtige Veröffentlichung von MILLER[4] über den Nachweis von Thallium mit Rhodamin B enthalten. Lediglich die Feststellung von GOTO[5], dass 3-wertiges Thallium die Fluoreszenz einer wässerigen Rhodamin B-Lösung von rot nach violett verschiebt, wodurch 0.5 γ Thallium nachweisbar sind, wird in dem Sammelreferat, nicht jedoch im Komissionsbericht erwähnt; es fehlt aber die Angabe, dass GOTO diesen Effekt, sowie auch die Auslöschung der Fluoreszenz von Rhodaminlösungen bei einer Reihe anderer Metallionen festgestellt hat[6]. MILLER verwendet das Reagens zur Identifizierung von Thallium im Verlaufe der systematischen qualitativen semimikro-Analyse, unter Zugrundelegung des Trennungsganges von NOYES UND BRAY[7]. Hierbei wird der durch Bromwasserstoffsäure erhaltene Niederschlag, der die Bromide von Silber, Blei und Thallium(I), sowie etwas basisches Wismutbromid enthält, zur Oxydation des Thalliums mit bromhältiger Bromwasserstoffsäure erwärmt und hierauf filtriert. Zu einem Tropfen des Filtrates, das $[TlBr_4]^-$-Ionen enthält, wird zur Einstellung einer entsprechenden Acidität je ein Tropfen $9N$ Bromwasserstoffsäure, Wasser und zur Entfernung des überschüssigen Broms verdünnte Lösung von Dinatriumarsenit zugesetzt. Zu der so erhaltenen farblosen Lösung wird tropfenweise ein geringer Überschuss einer 1%igen Lösung von Rhodamin B in $3N$ Bromwasserstoffsäure hinzugefügt. Ein violetter Niederschlag verweist auf die Anwesenheit von Thallium. Die Autorin gibt an, dass auf diese Weise in einem Gemenge von 0.25-10 mg Thallium neben 0.25-50 mg Silber und Blei das Thallium einwandfrei zu erkennen ist. Mit Rücksicht darauf, dass bei den Verfahren von MILLER und

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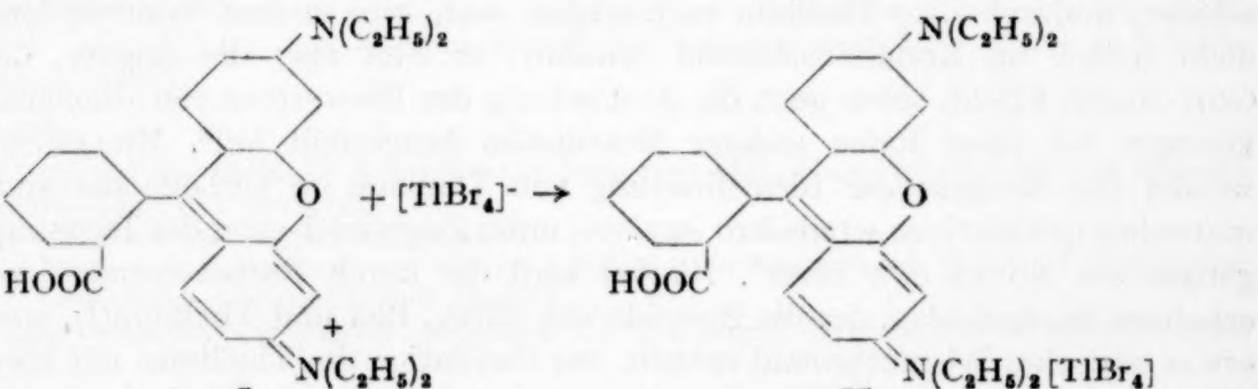
GOTO Tropfenreaktionen verwendet werden, erschien es wünschenswert, deren Erfassungsgrenze und Grenzverdünnung, sowie allfällige Beeinträchtigungen festzustellen. Bei diesbezüglichen Versuchen wurden einige neue Beobachtungen gemacht, die es ermöglichen, zu einem weitgehend selektiven und überaus empfindlichen Nachweis für Thallium zu gelangen, der auch in der Spurenanalyse verwendbar ist.

Wie bereits von EEGRIWE festgestellt worden ist, reagiert Rhodamin B in stark saurer Lösung unter Bildung violetter Niederschläge mit einer Reihe von Metallen, die als Bestandteile von Sauerstoffsäuren (Mo, W) oder als Bestandteile von komplexen Metallhalogensäuren (Sb(V), Tl(III), Hg, Au) fungieren, sowie mit konzentrierten Lösungen von Alkalirhodanid. Die lange unbekannte Aufklärung der Zusammensetzung des mit Rhodamin B gebildeten antimonhaltigen Niederschlages verdanken wir KUTZNIKOW[8]. Dieser Forscher hat den Umstand berücksichtigt, dass für das Zustandekommen der Antimon(V)-Reaktion die Anwesenheit von Chlorionen erforderlich ist, und daraus den richtigen Schluss gezogen, dass es sich um eine Reaktion von $[SbCl_6]^-$-Ionen handelt und der violette Antimon-Niederschlag ein Salz des basischen Farbstoffes mit Antimon(V) Chlorwasserstoffsäure ist. Die Annahme ist daher naheliegend, dass Fällungen, die mit Rhodamin B erfolgen, ganz allgemein auf der Bildung von Salzen dieses basischen Farbstoffes mit Anionen von normalen und Komplexsäuren beruhen.

Wenn wir dem Rhodamin B, bzw. dessen Farbstoff-Anion in saurer Lösung die Formel I zuweisen[9], dann gelangen wir bei der Einwirkung von $[TlBr_4]^-$-Ionen zur Umsetzung:



I II

Die durch obige Umsetzung gebildete Verbindung II ist das Tetrabromo-Thallium(III) Salz des Rhodamin B; analoge Verbindungen entstehen mit $[TlCl_4]^-$, $[AuCl_4]^-$, $[AuBr_4]^-$ etc. Ionen.

Wir fanden, dass die mit den komplexen Thallium(III)-Halogenionen gebildeten rot-violetten Niederschlägen im UV-Licht keine Fluoreszenz zeigen. Schüttelt man die stark salzsäure Farbstofflösung (die im UV-Licht weit weniger fluoresziert als schwach saure, neutrale oder alkalische Lösungen) mit Benzol aus, so ist keine Veränderung wahrnehmbar. Die Benzolschichte bleibt farblos und zeigt

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keine Fluoreszenz. Wird der Ausschüttelungsversuch mit den in Wasser, Salzsäure oder salzsauren Farbstofflösungen suspendierten Thallium(III)verbindungen ausgeführt, so erfolgt Lösung derselben im Benzol*. Die Benzolschichte nimmt eine intensiv rot-violette Farbe an** und zeigt im UV-Licht je nach der Niederschlagsmenge eine orangefarbene bis rötliche Fluoreszenz. Zur Hervorbringung der Fluoreszenz genügen bereits Thallium(III)mengen, die weder nach dem Verfahren von MILLER durch eine Niederschlagsbildung, noch nach dem Verfahren von GOTO (das in schwachsaurer Lösung ausgeführt wird) durch Änderung der Fluoreszenzfarbe nachweisbar sind. Auf der Bildung von in benzolischer Lösung fluoreszierenden Thalliumverbindungen lässt sich daher ein empfindlicher Thalliumnachweis begründen.

Ausführung. In eine Mikroeprouvette wird ein Tropfen der neutralen oder schwach sauren Thallium(I)lösung gebracht und ein Tropfen gesättigtes Bromwasser zugesetzt. Das unverbrauchte Brom wird durch Zusatz eines Tropfens einer wässerigen Lösung von Sulfosalicylsäure entfernt, was am Verschwinden der Gelbfärbung leicht zu erkennen ist. Durch dieses Verfahren werden Thallium(I)salze unter Bildung von $[TlBr_4]^-$-Ionen quantitativ oxydiert[11]. Hierauf wird ein Tropfen Rhodamin B-Lösung und 6-8 Tropfen reinstes Benzol zugesetzt und ausgeschüttelt. Bei Anwesenheit von Thallium fluoresziert die rote Benzolschichte im UV-Licht*** intensiv orange-rot.

Erfassungsgrenze. 0.03 γ Thallium
Grenzverdünnung. 1:1,660,000
Reagenzien. 1. Bromwasser
2. 10%ige wässerige Lösung von Sulfosalicylsäure
3. 0.05%ige Lösung von Rhodamin B in konz. Salzsäure
4. Reinstes Benzol

Da Rhodamin B als Fällungsmittel für Anionen bestimmter normaler und komplexer Metallsäuren fungiert, wurde das Verhalten von einschlägigen Anionen, sowie von Metallionen, die zur Bildung von komplexen Metall-Halogeno-Ionen befähigt sind, zu Rhodamin B und Benzol geprüft und hierbei die Bedingungen des oben beschriebenen Thalliumnachweises eingehalten. Die Versuche wurden als Tropfenreaktionen mit 0.2%igen Metallsalzlösungen ausgeführt, die demnach im Tropfen 100 γ Metall enthielten. In nachstehender Aufstellung sind die in der wässerigen Lösung dem Rhodamin gegenüberstehenden Ionenarten, sowie Farbe und Fluoreszenz der Benzolschichte angegeben:

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* In gleicher Weise wie Benzol verhält sich Äther und Amylalkohol, nicht jedoch Chloroform. Wird eine salzsaure Lösung von Rhodamin B mit Chloroform ausgeschüttelt, so zeigt die Chloroformschichte eine gelbe Fluoreszenz. Dadurch sind noch 0.5 γ Rhodamin B im Tropfen nachweisbar. Es ist wahrscheinlich, dass es sich bei diesem Effekt um die Freilegung und Extraktion des Farbstoffes aus der wässerigen Lösung des Chlorides handelt.

** In einer soeben erschienenen Publikation von C. L. LUKE[10], finden wir den Hinweis, dass von W. C. ALFORD (private communication) die Löslichkeit der Thallium(III) und Gold-Rhodaminverbindungen in Benzol beobachtet worden ist. Dieser Befund war uns bei Durchführung der hier beschriebenen Versuche nicht bekannt.

*** Bei den Versuchen wurde die Hanovia Inspectolyte Quarzlampe verwendet.

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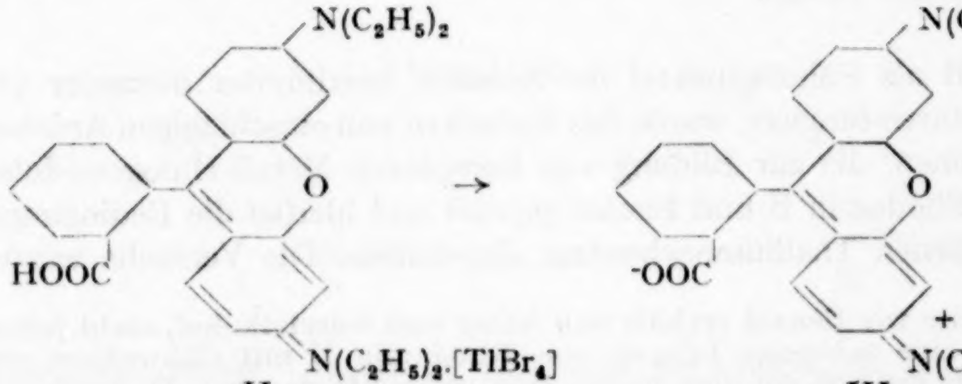
Farblose Benzolschichte: MoO_4^{-2}, WO_4^{-2}, $[PtCl_6]^{-2}$, $[PdCl_4]^{-2}$, $[RhCl_6]^{-3}$, $[RhBr_6]^{-3}$, $[IrCl_6]^{-2}$
$[IrBr_6]^{-2}$, Bi^{+3}, $[BiBr_4]^-$, Ce^{+3}, $[CeCl_4]^-$, $[CeBr_4]^-$, $[SbCl_4]^-$, $[SbBr_4]^-$-Ionen
Rote Benzolschichte ohne Fluoreszenz*: $[SbCl_6]^-$, $[SbBr_6]^-$, $[FeCl_6]^{-3}$, $[FeBr_6]^{-3}$-Ionen
Rote Benzolschichte mit orangefarbiger Fluoreszenz: $[TlCl_4]^-$, $[TlBr_4]^-$, $[AuCl_4]^-$, $[AuBr_4]^-$, CNS^-, Hg^{+2}, $[HgCl_4]^{-2}$, $[HgBr_4]^{-2}$-Ionen

Obige Versuche sind streng reproduzierbar. Bei Verminderung der Acidität, Erhöhung der Konzentration der Reagenslösung und der betreffenden Metallsalzlösung ist zu beachten, dass das Reaktionsbild vom obigen Schema mitunter abweichen kann.

Ohne Behandlung mit Bromwasser liefern saure Alkalirhodanidlösungen nach Zusatz von Rhodamin B und Ausschuetteln mit Benzol eine rotviolette Benzolschichte, die im UV Licht orange fluoresziert. Die von West und Hamilton[14] einem Antimonnachweis zugrundegelegte Additionsverbindung von Antimon(III) Jodid und Rhodamin B, deren benzolische Lösung eine rotviolette Farbe besitzt, zeigt im UV Licht keine Fluoreszenz.

Nach dem bisher vorliegenden Beobachtungsmaterial ist für das Zustandekommen einer Fluoreszenz nicht nur die Löslichkeit von Rhodaminverbindungen in Benzol mit roter Farbe erforderlich. Die Annahme ist naheliegend, dass die Fluoreszenz mit einer Änderung der Bindungsweise des Rhodamins zusammenhängt. Im Falle des Vorliegens der Thallium(III)bromidverbindung als hierhergehöriges Beispiel könnte folgende Umlagerung in Betracht gezogen werden:



II III

Die Verbindungen II und III sind zueinander isomer. Möglicherweise kommen die beiden Formen als Resonanzformen in Betracht, und es beruht das Auftreten der Fluoreszenz auf Resonanz.

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* Die Löslichkeit der Antimon(V)-Rhodaminverbindung in Benzol ist zuerst von Webster und Fairhall[12] festgestellt worden, sie bildet die Grundlage für die kolorimetrische Bestimmung kleiner Antimonmengen[13].

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Das Verhalten von Metallsalzlösungen gegen Rhodamin unter den Bedingungen des Thalliumnachweises zeigt, dass Beeinträchtigungen dieses Nachweises lediglich bei Anwesenheit von Gold-, Quecksilber- sowie Antimon(III)- und -(V)salzen zu erwarten sind. Gold- und Quecksilbersalze stören durch die Bildung fluoreszierender Benzolschichten. Grössere Mengen von Antimon(V)salze beeinträchtigen den Thalliumnachweis durch den Verbrauch von Rhodamin B, wodurch die Bildung der in benzolischer Lösung fluoreszierenden Thallium(III)-Rhodaminverbindung unterbliebt. Es sind deshalb für den Nachweis von Thallium neben den genannten Metallen besondere Massnahmen erforderlich. Eine Beeinträchtigung des Thalliumnachweises durch die Anwesenheit von Rhodanid ist nicht zu befürchten, weil bei der Oxydation von Thallium(I) zu Thallium(III) durch überschüssiges Bromwasser Rhodanide unter Bildung von Sulfat und Dicyan quantitativ zersetzt werden.

Nachweis von Thallium neben Antimon, Gold und Quecksilber

Soll Thallium neben Antimon, Gold und Quecksilber nachgewiesen werden, so ist die saure Probelösung mit Kupfer- oder Messingdraht zu behandeln. Hierbei werden Gold, Quecksilber und Antimonsalze zu den entsprechenden Metallen reduziert, die auf dem Messing als Belage hinterbleiben. Thallium(I)salze bleiben unverändert; im Falle des Vorliegens von Thallium(III)salzen werden diese zu Thallium(I)salzen reduziert.

Ausführung. In einer Mikroeprouvette wird ein Tropfen der Probelösung gebracht, ein Tropfen konz. Salzsäure zugesetzt und ein dünner Kupfer- oder Messingdraht, der an seinem Ende zu einer Spirale ausgebogen ist, eingehängt. Man belässt die Eprouvette ca. 5 Minuten in siedendes Wasser und zieht hierauf den Metalldraht aus der Lösung. Falls diese durch Metallfilter getrübt ist, muss filtriert oder zentrifugiert werden. Die klare Lösung wird nach Zusatz von Bromwasser, Sulfosalicylsäure, etc. in der bereits angegebenen Weise auf Thallium geprüft.

Mit Hilfe des oben beschriebenen Verfahrens waren einwandfrei nachweisbar: 0.1 γ Thallium neben 500 γ Gold, Quecksilber, Antimon.

Nachweis von Thallium in extrem verdünnter Lösung

In Lösungen unterhalb der Grenzverdünnung des Thalliumnachweises mit Rhodamin B kann das Thallium nicht unmittelbar nachgewiesen werden, sondern es ist vorher Anreicherung des Thalliums an einen geeigneten Kollektor erforderlich. Das Standardwerk über Spurenanalyse von SANDELL[15] enthält Hinweise auf Kollektorwirkungen von Metallsulfiden, sowie Eisenhydroxyd und Mangandioxyd. Wir fanden, dass für unsere Zwecke die Fällung von Braunstein am besten geeignet ist, um enorm verdünnten Lösungen das Thallium als Thallium(III)hydroxyd oder als Thallium(III)manganit zu entziehen. Isoliert man

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den Niederschlag, so kann nach dessen Auflösung in schwefeldioxydhaltiger Salzsäure das Thallium nach Oxydation durch die Fluoreszenzreaktion mit Rhodamin B bequem nachgewiesen werden.

Ausführung. Zu der auf Spuren von Thallium zu prüfenden Lösung werden je nach dem verwendeten Volumen (20-500 ml) 0.5-3 ml einer 0.1%igen Lösung von Mangansulfat und hierauf Bromwasser bis zur deutlichen Gelbfärbung zugesetzt. Die Lösung wird nach Zusatz eines geringen Überschusses von Natronlauge zum Sieden erhitzt. Der hierbei abgeschiedene Braunstein wird auf einem Filter gesammelt, einmal mit heissem Wasser gewaschen und hierauf mit 1 ml Salzsäure (1:1) dem einige Kriställchen Natronsulfit beigemengt werden, übergossen. Das Filtrat wird in einer Mikroeprouvette gesammelt, und zur Vertreibung der überschüssigen schwefligen Säure einmal aufgekocht. Zur erkalteten Lösung wird tropfenweise Bromwasser bis zur bleibenden Gelbfärbung zugesetzt, durch einen Tropfen 10%iger Sulfosalicylsäure überschüssiges Brom entfernt und hierauf ein Tropfen einer 0.2%igen wässerigen Lösung von Rhodamin B und 20 Tropfen Benzol zugesetzt. Nach Ausschütteln ist die Benzolschichte rot und zeigt im UV-Licht eine orangefarbene Fluoreszenz, wenn Spuren Thallium in der Probelösung enthalten sind. Nach obigem Verfahren war 0.1 γ Thallium in 500 ml Wasser einwandfrei nachweisbar. Dies entspricht einer Nachweisbarkeit von Thallium in der Verdünnung 1:5,000,000,000.

Wir danken an dieser Stelle dem Conselho Nacional de Pesquisas für die Unterstützung bei der Durchführung dieser Arbeit.

ZUSAMMENFASSUNG

Die Rhodaminverbindungen von Thallium(III)chlorid und -bromid sind in Benzol mit roter Farbe löslich. Die Benzollösung fluoresziert im UV-Licht orangerot. Der Chemismus der Fluoreszenreaktion wird diskutiert.

Es wird die Ausführung eines Thalliumnachweises mit Rhodamin B als Tüpfelreaktion beschrieben. Die erreichte Erfassungsgrenze beträgt 0.03 γ Thallium. Bei Anwesenheit von Gold-, Quecksilber und Antimonsalzen ist der Nachweis nicht unmittelbar anwendbar. Es wird ein Verfahren zur Beseitigung der störenden Metallionen beschrieben.

Durch die Rhodaminreaktion ist ein Nachweis von 0.1 γ Thallium in 500 ml Wasser möglich, was einer Verdünnung $1:5\cdot10^9$ entspricht.

SUMMARY

The combinations of rhodamine with thallium(III) chloride or bromide are soluble in benzene giving a red coloration. This solution shows an orange-red fluorescence in ultraviolet light. The mechanism of the fluorescent reaction is discussed.

A method for the detection of thallium with rhodamine B in form of a drop test is described. The limit of identification is 0.03 γ Tl. In the presence of gold, mercury and antimony salts, the direct application of the test is not possible. A procedure for the elimination of the interfering metallic ions is given.

By means of the reaction with rhodamine it is possible to demonstrate 0.1 γ Tl in 500 ml water, which corresponds to a dilution of $1:5\cdot10^9$.

Literatur S. 399.

RÉSUMÉ

Les combinaisons rhodamine-chlorure ou bromure de thallium(III) sont solubles en rouge dans le benzène. Cette solution présente une fluorescence orange rouge en lumière ultraviolette. Le mécanisme de la réaction fluorescente est discuté.

Une méthode ,,à la touche" est décrite pour déceler le thallium avec la rhodamine B. On peut atteindre une limite de sensibilité de 0.03 γ Tl. Les sels d'or, de mercure et d'antimoine gênent la réaction. On décrit un procédé d'élimination des ions métalliques gênants.

Au moyen de cette réaction [illegible] la rhodamine B, il est possible de déceler 0.1 γ Tl dans 500 ml d'eau, ce qui correspond à une dilution de $1:5 \cdot 10^9$.

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MATERIALERSPARNIS, ZEITGEWINN UND ERHÖHTE GENAUIGKEIT IN DER MASSANALYSE DURCH „UMKEHRTITRATIONEN"

von

F. L. HAHN

Durango 283, México 7, D.F. (México)

Sollen bei Gewichtsanalysen Kontrollbestimmungen ausgeführt werden, so müssen wir wohl oder übel für jede Wiederholung ungefähr die gleiche Menge Material, Reagentien und Arbeit opfern; dasselbe tun wir gewohnheitsmässig auch bei massanalytischen Arbeiten, obwohl es hier völlig unnötig und durchaus weckwidrig ist. Ein wesentlich vorteilhafteres Verfahren soll im folgenden zeschrieben werden, der Einfachheit halber unter Verwendung konkreter Zahlen; wie diese unter veränderten Bedingungen abzuändern sind, bedarf keiner Erklärung.

Man messe die Substanzlösung nicht mit der Pipette sondern fülle auch sie in eine Bürette von 25 ml; es ist vorteilhaft, (siehe unten: Fehler von Messgefässen), stets die gleiche zu verwenden; an Substanzlösung, um die Bürette notfalls vorzuspülen, wird nie Mangel sein.

Nun legt man 15-19 ml Substanz vor, ohne sie genau abzumessen, und titriert *rasch* auf Umschlag; nur wenn ein Reagensüberschuss etwa zersetzt wird (z.B. Thiosulfat beim titrieren von stark sauren Lösungen), muss man sich vor stärkerem Übertitrieren hüten. Man gibt nun mehr Substanz zu, diesmal genau gemessen bis zu einem passenden Volumen, z.B. 20 ml, und titriert auf genauen Umschlag; auch das geht rasch, da man ja bereits einen Näherungswert hat. — Man gibt 0.5 ml mehr Substanz zu und titriert wieder zum genauen Umschlag, und so fort bis man eine genügende Zahl Äquivalenzwerte hat; die Summe aller Reagensvolumina durch die Summe aller Substanzvolumina ergibt den Mittelwert der Bestimmung. Es ist leicht, in kürzester Zeit soviele Einzelwerte zu haben, dass die im Mittel erreichte Genauigkeit aus den Fehlerquadraten errechnet werden darf.

Dass dies Verfahren eine bedeutende Zeitersparnis mit sich bringt ist klar: es sind jeweils nur wenige Zehntel-Milliliter tropfenweise zu titrieren. Ebenso, dass es die erreichbare Genauigkeit erhöht: misst man mit einer 25 ml-Pipette, so reichen 50 ml gerade für 2 Bestimmungen, während nun 25 ml für 11 Bestimmungen genügen, und da zur Mittelbildung alle Volumina addiert werden, sollte die prozentuale Unsicherheit einigen Hundertstel Milliliter auf 300 ml Verbrauch entsprechen; die Versuche haben das bestätigt*.

Bis hierher handelt es sich um eine Änderung in der Arbeitstecnik, die nur deshalb zu einer erhöhten Analysier-Genauigkeit führt, weil sie eine grössere Zahl von Einzelbestimmungen ermöglicht. Gehen wir nun zu der Form des Verfahrens über, für die der Name „Umkehrtitrationen" geprägt ist, so erhalten wir überdies ein Forschungswerkzeug, das in einfachster Form Probleme löst, die bisher nur schwer und umständlich zu behandeln waren. Die grosse Mehrzahl der Titrationen ist umkehrbar, das heisst, Stoff und Reagens können in ihrer Funktion vertauscht werden. In solchen Fällen titriert man zweckmässig, wie beschrieben, mit dem Reagens zum ersten Äquivalenzwert der „R-Reihe", gibt nun einen kleinen Reagensüberschuss zu (bis zum nächsten vollen oder halben Milliliter), titriert mit Substanz zurück bis zum ersten Äquivalenzwert der „S-Reihe", und sofort. „Paarwerte" wollen wir die Quotienten nennen, die in folgender Weise erhalten wurden: Man summiert die beiden Substanz-Volumina der ersten Hin- und Rücktitration und ebenso die beiden Reagens-Volumina und bildet den Quotienten dieser Summen. Mittelwerte erhalten wir wieder: Für die R-Reihe, bei der mit Reagens austritriert wurde, durch Summieren aller entsprechenden Substanzvolumina und Reagensvolumina und Division; ebenso für die S-Reihe, bei der mit Substanz zurücktitriert wurde; und Mittel der Paarwerte ist der Quotient aus den Summen von Reagens — durch Substanz-Volumina beider Reihen.

Welche Übereinstimmung oder welche Abweichungen haben wir für diese drei Klassen von Äquivalenzwerten zu erwarten? Es darf angenommen werden, dass beim Titrieren mit Reagens ein kleiner Überschuss an diesem verbraucht werden muss, um den Umschlag erkennbar zur machen, ebenso beim Rücktitrieren ein kleiner Überschuss an Substanz. Es sollte also in der R-Reihe die analysierte Lösung etwas stärker und in der S-Reihe etwas schwächer erscheinen, als sie tatsächlich ist, und die Paarwerte sollten der tatsächlichen Äquivalenz zum mindesten ganz ausserordentlich nahekommen; im Idealfalle müssen sie ihr sogar gleich sein. Die Grösse des Unterschiedes zwischen den „Gegenreihen" lässt sich aus einfachen Überlegungen abschätzen, und die Beobachtung stimmt mit der theoretisch zu erwartenden Abweichung überein immer dort, wo Abweichungen von der stöchiometrischen und unmessbar schnellen Umsetzung nicht zu erwarten sind.

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* Die Ablesegenauigkeit ist für die Einzelmessung bei der Bürette etwas geringer als die Messgenauigkeit einer guten und völlig klar auslaufenden Pipette. Dafür müssen sich aber bei zahlreichen Bürettenablesungen die Schätzungfehler weitgehend ausgleichen, und zwar für normale und erfahrene Beobachter schon dadurch, dass sie gleich oft und gleich stark nach oben und unten abweichen. Aber selbst für Beobachter, die einseitig zu hohe oder zu tiefe Schätzungen bevorzugen, muss sich dieser Fehler an der Substanz- und Reagens-Bürette gleichmässig auswirken, und ganz sicher fällt er heraus, wenn Einstellung der Masslösung und Analyse in der gleichen Form und mit denselben Büretten durchgeführt werden.

In vereinzelten Fällen wurde schon bisher mit Substanz in die Reagenslösung titriert. Ein bekanntes Beispiel hierfür ist die Bestimmung von Nitrit mit Permanganat, die bei erhöhter Temperatur und in saurer Lösung durchgeführt werden muss; da eine Nitritlösung beim Ansäuern zersetzt wird, titriert man mit dem Nitrit in das vorgelegte, angesäuerte, stark verdünnte Permanganat auf Entfärbung. Man muss sehr langsam titrieren, denn die Zersetzung des Nitrits durch Säure geht rascher als seine Oxydation, sobald die Konzentration nicht sehr klein ist; es darf also niemals viel Nitrit auf einmal zugegeben werden. Bei den Kontrollbestimmungen werden nun, statt weitere 25 oder 50 ml Permanganat zu reduzieren, nur wenige Tropfen von diesem zugegeben, die erneut auf Entfärbung titriert werden; dass der Zeitgewinn hier ganz ausserordentlich ist, steht fest*.

In andern Fällen, z.B. bei der Titration von Ferrosalz mit Dichromat (Diphenylamin oder -benzidin als Redoxindikator) oder von Zink mit Ferricyanid-haltigem Ferrocyanid (ebenso) ist der Umschlag nicht scharf, wenn mit dem Reagens titriert wird; es wird daher empfohlen, von diesem einen Überschuss zuzugeben, der dann mit einer Normal-Lösung von Eisen oder Zink zurückgemessen werden soll. Benutzt man statt dessen eine Bürette zum Messen der Substanzlösung, so kann man ohne weiteres mit dieser fertigtitrieren, spart also die Verwendung einer zweiten Masslösung und hat wieder den Vorteil, eine grosse Zahl von Umschlägen und Äquivalenzwerten mit wenig Material und in kürzester Zeit zu erhalten.

Diese Möglichkeit, eine grosse Anzahl von Äquivalenzwerten zu erhalten und dabei zu vergleichen, wie die scheinbare Äquivalenz der beiden beteiligten Lösungen sich ändert, je nachdem in der einen oder der anderen Richtung titriert wird, ist von unschätzbarem Wert für das genaue Studium problematischer Titrierungen. Für Reaktionen, deren Vollständigkeit und völlige Umkehrbarkeit sicher ist, z.B. Säure gegen Lauge, beide stark, lässt sich die zwischen den Gegenreihen zu erwartende Differenz errechnen, und die Versuche haben die Erwartung bestätigt. (Siehe: Versuchsergebnisse.) Finden wir in weniger einfachen Fällen dieselbe Richtung und Grösse in den Unterschieden, so können wir schliessen, dass es sich auch hier um vollständige und vollkommen reversible Titrier-Reaktionen handelt. Dies wurde bestätigt für die Titration von Chlorid gegen Silber nach Mohr (neutrale Lösung, Chromat als Indikator); *kleine* Silberüberschüsse lassen sich gut auf Entfärbung titrieren. Bei der Volhard-Titration, Rücktitration eines Silberüberschusses mit Rhodanid bei Gegenwart von AgCl als Bodenkörper, konnte gezeigt werden, dass die Eisenrhodanid-Färbung unter bestimmten Bedingungen stabil wird (tatsächlich stabil, nicht stabilisiert durch Umhüllen des ausgefallenen AgCl).

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* Es liegt der Einwand nahe, dass es gerade in diesem Fall wichtig und nötig sein könne, auch den ersten Teil der Bestimmung zu wiederholen, weil schon in ihm, durch unregelmässigen Reaktionsverlauf, Abweichungen entstehen könnten. Wie alle nach dem üblichen Verfahren durchgeführten Bestimmungen gezeigt haben, ist dies nicht der Fall, wenn folgende, leicht einzuhaltende Bedingungen beachtet werden: Dauerndes, am besten mechanisches Rühren; jetzt besonders leicht durchführbar, seit die elektromagnetischen Rührer die Öffnung des Titriergefässes völlig frei lassen. — Stetiger und sehr langsamer Zufluss der Nitritlösung; man verlängere die Bürettenspitze seitlich durch einen „Schwanenhals" mit sehr fein ausgezogener Spitze, so dass auch bei voll aufgedrehter Bürette die Lösung etwa 1-2 ml in der Minute ausläuft. Damit kommt die Bürette zugleich aus der Erwärmung über der titrierten Lösung heraus. Die Auslaufspitze kann so weit verlängert werden, dass das Nitrit nicht auf die Oberfläche der Lösung auftropft sondern in ihre unteren Schichten einströmt; das scheint aber nicht einmal nötig zu sein. — Man stelle neben die titrierte Lösung ein gleiches Gefäss mit einem gleichen Volumen Wasser, das durch 1-3 Tropfen Permanganat angefärbt ist; dann genügt ein rascher Blick nach dem ohne Wartung laufenden Versuch, um festzustellen, ob er sich dem Endpunkt nähert. Man kann in dieser Weise auch auf Farbgleichheit mit einer schwach angefärbten Lösung statt auf völlige Entfärbung titrieren; dann kann nie ein Nitritüberschuss auftreten.

Bei der Härtebestimmung in Wässern mit Komplexon-Lösung als Reagens und Eriochromschwarz T als Indikator werden wesentliche Verbesserungen erreicht, wenn zunächst mit Wasser in das Reagens titriert wird; nach dem ersten Umschlag kann die Titration beliebig oft wiederholt und die Genauigkeit der Bestimmung auf jeden gewünschten Wert gesteigert werden, was für Wasser-

TABELLE I

UMKEHRTITRATIONEN VON SCHWEFELSÄURE GEGEN NATRONLAUGE

Beide Lösungen etwa N/10. — Indikator: Methylrot.
Titriert wurde in den A-Reihen: Säure mit Lauge.
in den B-Reihen: Lauge mit Säure.

ml H_2SO_4		ml NaOH		10 ml Säure = 9.xxx ml Lauge		
A	B	B	A	A	B	Paare
30	30.65	30	29.40	800	788	794
31	31.62	31	30.38	800	804	802
32	32.70	32	31.29	781	786	782
33	33.72	33	32.30	788	786	787
34	34.80	34	33.26	782	770	776
35	35.81	35	34.21	774	774	774
36	36.83	36	35.20	776	774	776
37	37.83	37	36.20	784	775	782
38	38.84	38	37.15	784	780	789
39	39.90	39	38.13	777	784	776
					774	
345	352.70	345	337.55	9.7840	9.7814	
697.70		682.55		Paare:		9.7828

Aus den Abweichungen der Einzelquotienten von den Mittelwerten (Summenquotienten) errechnet sich in allen drei Reihen ein mittlerer Fehler des Summenquotienten (Analysenergebnis) von weniger als 0.0003 ml, entsprechend einer Analysengenauigkeit von ± 0.003%.

analysen kaum wichtig ist, wohl aber für die Bestimmung der Erdalkalien in Blutserum und ähnliche Fälle. Bei dieser Titration wurde ein anormales Verhältnis der Äquivalenzwerte aus den Gegenreihen beobachtet, für das eine einleuchtende Erklärung gegeben werden kann; Einzelheiten derartiger Anwendungen sollen weiterhin gegeben werden.

Schliesslich hat sich gezeigt, dass Umkehrtitrationen sich vorzüglich zur Bürettenprüfung eignen. Bei einer der vorstehend angegebenen Untersuchungen wurden Abweichungen in den Stärkequotienten gefunden, die durch keine Theorie erklärbar waren. Die Abweichungen blieben bestehen, als die problematischen Lösungen durch normale Salzsäure und Natronlauge ersetzt wurden, und sie kehrten sich um, als die Büretteninhalte vertauscht wurden. Es war nun ein einfaches Problem der Kompensationsrechnung, wieviel zu jeder einzelnen Volumenablesung addiert oder von ihr subtrahiert werden müsse, um den „Gang" zu eliminieren und eine möglichst geringe Streuung der Einzelwerte zu erhalten. Die so gefundenen Korrekturen konnten durch Auswägen der Büretten bestätigt werden (Fig. 1). Derartig erstaunliche Fehler wurden nur an einem Bürettenpaar gefunden.

VERSUCHSERGEBNISSE UND IHRE DEUTUNG

Die Ergebnisse von Umkehrtitrationen werden zweckmässig in der Form aufgeschrieben, die aus Tabelle I hervorgeht.

Es wurden im ersten Versuch 30 ml Säure vorgelegt und 29.40 ml Lauge verbraucht (Quotient: 1 ml Säure = 0.9800 ml Lauge), dann Lauge bis 30 ml zugegeben und mit Säure zurücktitriert (Verbrauch: 30.65 ml; Quotient: 0.9788); die Summe beider Laugenmengen (59.40 ml) durch die Summe der Säuremengen (60.65 ml) gibt den ersten der unter „Paare" aufgeführten Quotienten: 0.9794.

In den letzten Zeilen sind die Summen aller abgelesenen Volumina gegeben; ihre Quotienten entsprechen den Mitteln der drei Reihen, wenn die „Gewichte" der Einzelwerte, wie üblich und berechtigt, proportional den Volumina gesetzt werden.

Dass jeweils die Lösung, mit der titriert wird, das „Reagens" (dies hier ohne Rücksicht darauf, welche Lösung analysiert wird), etwas schwächer erscheint, ist selbstverständlich; nur in Ausnahmefällen kann ja der Äquivalenzpunkt genau mit dem Ende eines Tropfens zusammenfallen. In der Regel muss vom letzten Tropfen, der den Umschlag bringt, ein geringer Bruchteil bis nahezu die ganze Menge Überschuss sein (je nachdem, ob nach dem vorangehenden Tropfen, der noch nicht zum Umschlag führte, fast ein voller Tropfen oder nur sehr wenig an Äquivalenz fehlte). Im Durchschnitt wird daher von dem Reagens je Bestimmung etwas weniger als ein halber Tropfen im Überschuss zugegeben, und wenn wir von den Summen der Lösungsvolumina bei n Bestimmungen etwas weniger als n/2 Tropfen abziehen, sollten die Quotienten der beiden „Gegenreihen" auf den Quotienten der „Paarwerte" kommen. Der hier gefundene Unterschied ist merklich kleiner; es genügt, von den Summenwerten der Reagensvolumina 0.04 ml abzuziehen, damit die Quotienten: 337.51:345 und 345:352.66 dem Quotienten der Paarwerte: 0.97828 gleich werden. Der Grund hierfür liegt darin, dass bei diesen Versuchen am Endpunkt vielfach nicht ganze Tropfen sondern kleine Bruchteile eines Tropfens zugesetzt wurden (z.B. durch Abtupfen der Menge, die noch an der Bürettenspitze hing), wenn der Eindruck bestand, dass die Lösung gerade am umschlagen war; die Versuche wurden von einem geübten Beobachter durchgeführt, der den Umschlag kommen sieht, und es wurde sorgfältig mit Lauge auf praktisch rein gelb und mit Säure auf eben erkennbare Abweichung von reinem gelb titriert. Unerfahrene Beobachter und vor allem solche, die sich nicht davon frei machen können, dass man auf vollen Umschlag titrieren müsse, finden etwas grössere Unterschiede; ein Student brauchte bei der ersten Titration, die er je ausführte, 0.023 ml Reagensüberschuss je Bestimmung bei einer mittleren Tropfengrösse von 0.04 ml. Dabei wurden unter Verwendung von 2 Büretten von 25 ml Inhalt 10 Titrationspaare erhalten; aus den Abweichungen der Einzelwerte errechnet sich der Fehler des Mittels zu ± 0.045%.

Nichts kann deutlicher als dieses Ergebnis die grossen Vorteile zeigen, die „Umkehrtitrationen" auch im Unterricht mit sich bringen. Der Anfänger kann bei jedem ihm neuen Verfahren, ohne Sorge um Materialverlust durch übertitrieren, den Umschlag kennen lernen und fängt mit dem Aufschreiben von Ablesungen erst dann an, wenn er sich sicher fühlt; das tropfenweise titrieren, noch 5 oder 10 ml vom Umschlag entfernt, fällt fort.

Für den Geübten und bei hohen Ansprüchen an Genauigkeit sei bemerkt: Selbstverständlich darf die erste Ablesung, vor der ja eine grössere Reagensmenge recht rasch zugegeben wurde, erst nach gebührender Nachlaufzeit gemacht werden; bei den weiteren, mit 0.5 bis 1 ml zusätzlichen Reagensmengen, ist der Nachlauf natürlich ohne jeden Einfluss.

DIE PRÜFUNG VON MESSGEFÄSSEN

Büretten werden heutzutage nach Verfahren hergestellt, die im Extremfalle zu völlig konstantem Verhältnis zwischen Länge und Volumen führen, z.B. 1 cm Länge = 1 ml Inhalt; dass es nötig sein könne, die Genauigkeit des Gesamtvolumens oder gar die Proportionalität der Teilung nachzuprüfen, daran wird oft nicht gedacht. Und es muss zugegeben werden: Zwingt man eine ganze Generation von Anfängern im massanalytischen Praktikum, ihre Büretten zu „prüfen", mit dem Erfolg, dass kein einziger einen Fehler findet (und sie wissen, dass auch in früheren Jahren keiner gefunden wurde), so erhöht das nicht die Arbeitsfreudigkeit.

Gibt man statt dessen als erste Praktikumsaufgabe die Vergleichung von

Natronlauge und Salzsäure durch Umkehrtitrationen, so lehrt das Ergebnis, hinsichtlich der Schüler:

Die Sicherheit der Beobachtung; sie ist um so grösser, je weniger in jeder der Reihen die Einzelwerte vom Mittel abweichen.

Die Neigung zum übertitrieren; sie ist um so geringer, je weniger die Mittelwerte der beiden Gegenreihen auseinanderfallen.

Und hinsichtlich der Büretten, wenn man diese Versuche bei 5 ml beginnen und in Intervallen von etwa 2 ml fortsetzen lässt: das gelegentlich doch Abweichungen von Soll-Volumen vorkommen, die grösser sind als die bei dieser Arbeitsweise leicht zu erreichende Genauigkeit. Es wird dann ein „Gang" im Stärkeverhältnis der Lösungen gefunden (statt der normalen Streuung der Einzelwerte), wie z.B.

bei	5	10	15	20	25 ml HCl
1 ml HCl =	1.013	1.014	1.005	1.002	1.001 ml NaOH

Nun wurden die Büretteninhalte vertauscht, und damit kehrte sich das scheinbare Stärkeverhältnis der Lösungen um, so dass jetzt die Natronlauge stärker zu sein schien, während tatsächlich die Lösungen genau äquivalent

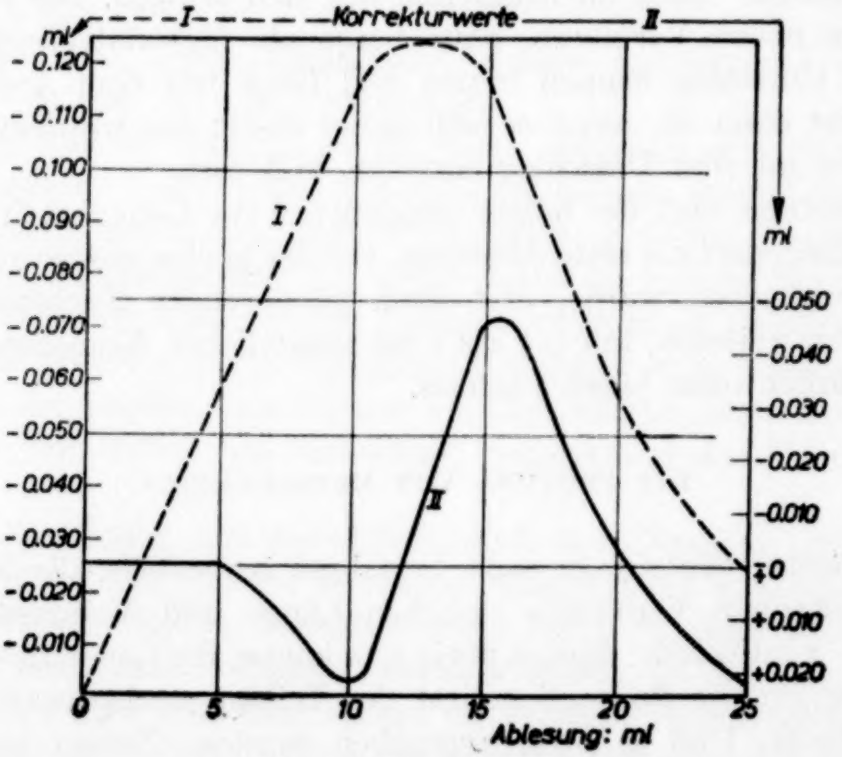

Fig. 1. Bürettenfehler.

Bei einer „Umkehrtitration" schien eine der Lösungen mit steigenden Volumina ständig stärker zu werden, und dieser „Gang" blieb erhalten, als nun Salzsäure gegen Natronlauge titriert wurde; er konnte also nur an Fehlern des verwendeten Bürettenpaares liegen. Aus der letzten Titration wurde errechnet, und dies wurde durch Auswägen der Büretten bestätigt, dass die Ablesungen durch die in der Graphik angegebenen Werte zu korrigieren sind.

waren. Auswägen der Büretten ergab für die erforderlichen Korrekturen die in Fig. 1 gegebenen Werte. Bringt man diese an den Ablesungen der Titrierwerte an, so zeigen die Quotienten nur die unvermeidlichen Streuungen; der Gang verschwindet.

Beispiele für den Wert des Verfahrens beim theoretischen Studium von Titrationsverfahren werden folgen.

ZUSAMMENFASSUNG

Wird bei Massanalysen auch die Substanzlösung mit der Bürette gemessen (statt wiederholt gleiche Mengen von ihr zu pipettieren), so reichen kleine Volumina Substanz für eine sehr grosse Zahl von Kontrollbestimmungen aus; das Mittel aller Bestimmungen zeichnet sich durch eine sonst nicht zu erreichende Genauigkeit aus, und die Arbeitszeit wird merklich verkürzt. Zugleich unterrichtet dieses Verfahren sofort über die Zuverlässigkeit der verwendeten Büretten.

SUMMARY

If, in volumetric analysis, the solution, as well as the reagent, is measured by means of a burette (replacing the usual pipette), we are able, after reaching the first end-point, to add a small quantity of either solution, substance or reagent, to titrate for a second end-point and to repeat these operations as many times as are necessary to obtain an average value with the desired accuracy, which can be very high. The economy, both in the amount of solution required and time, is considerable. The procedure is very useful in theoretical studies on controversial volumetric reactions and in calibrating burettes.

RÉSUMÉ

En mesurant la solution à analyser au moyen d'une burette (au lieu de la pipette ordinaire), ainsi que la solution de réactif, on peut ajouter après le premier virage, un petit volume d'une des 2 solutions (solution à analyser ou réactif) et titrer par l'autre jusqu'au second virage. On répète cette opération autant de fois qu'il faut pour obtenir, dans la moyenne de toutes ces opérations, la précision désirée, qui peut être très élevée. L'économie de solutions et l'économie de temps sont considérables. Ce procédé convient particulièrement bien à l'étude de réactions titrimétriques douteuses; il sert également à calibrer les burettes.

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THE COMPLEXOMETRIC DETERMINATION OF ZINC IN THE PRESENCE OF LARGE QUANTITIES OF MAGNESIUM

by

E. G. BROWN AND T. J. HAYES

Research and Development Department, British Enka Limited, Liverpool (England)

Previous work by the present authors[1] has shown that zinc and magnesium may be simultaneously titrated using disodium dihydrogen ethylenediamine tetra-acetate (Complexone III) and a differential pH buffering technique. We attempted to apply this method to the determination of zinc in the presence of a large excess of magnesium (molecular ratio of magnesium to zinc about 25:1) but no definite end-point for the titration of zinc at pH 6.8 could be obtained. The original procedure had been tested for molecular ratios of zinc to magnesium between the limits 3:1 and 1:3; consequently work was put in hand to determine the practical limits of this differential pH technique. Reasonably sharp end-points and quantitative recoveries were obtained up to a molecular ratio of magnesium to zinc of 5:1; thereafter end-points were indistinct. Apparently, however, a large amount of zinc may be successfully titrated in the presence of a small quantity of magnesium; for example, a molecular ratio of zinc to magnesium of 25:1 was quantitatively determined by initial titration of zinc at pH 6.8 and subsequent titration of magnesium at pH 10.

Use of potassium cyanide as complexing agent for zinc

In order to extend the range of analysis the use of the complexing action of potassium cyanide upon zinc ions was studied as a basis for an alternative procedure. Potassium cyanide has been used as a masking agent for the elimination of interference by heavy metals in complexometric methods by various authors, for example, SCHWARZENBACH AND BIEDERMANN[2], BETZ AND NOLL[3], DIEHL, GOETZ AND HACH[4], FLASCHKA AND HUDITZ[5], MCCOY[6]. In our experience, however, the use of potassium cyanide to mask relatively large quantities of zinc in the presence of magnesium led to high results for the magnesium determination and a gradual deterioration in the end-point with increase in zinc concentration. This phenomenon may be due to the comparable stabilities of the zinc cyanide complex and the chelate of zinc and Complexone III, the logarithms of the stability constant of these being 16.9 and 16.2 respectively.

The results obtained for a magnesium solution containing various quantities of zinc and potassium cyanide are shown in Table I.

TABLE I

THE EFFECT OF CYANIDE ION ON THE TITRATION OF MAGNESIUM IN THE PRESENCE OF ZINC

Series A. Solution containing 10 ml of 0.0248M Mg^{+2} solution and 10 ml of 2.5% KCN solution. Theoretical titre of 0.01M Complexone III solution 24.80 ml.

ml 0.0025M Zn^{+2} solution	ml 0.01M Complexone III solution	Remarks
0.00	24.90	
0.10	24.92	
0.20	24.93	
0.50	24.93	
1.00	24.95	End-point slightly vague
5.00	24.98	
10.00	25.11	End-point vague
15.00	25.25	
20.00	25.40	End-point very vague End-point returns

Series B. Solution containing 10 ml of 0.0248M Mg^{+2} solution + 20 ml of 2.5% KCN solution. Theoretical titre of 0.01M Complexone III solution 24.80 ml.

ml 0.0025M Zn^{+2} solution	ml 0.01M Complexone III solution	Remarks
10.00	24.96	End-point slightly vague
15.00	24.98	
20.00	25.01	End-point vague
40.00	25.15	

Use of Amberlite IR-120 for separation of zinc and magnesium

From the results shown in Table I it can be seen that a volumetric determination using moderate quantities of potassium cyanide is impracticable for comparable amounts of zinc and magnesium in admixture. It seemed, however, that the formation of a zinc cyanide complex in which the zinc forms part of the anion presented a ready means of separating zinc from magnesium even when the latter was present in large excess. This separation was achieved using a synthetic cation exchange resin. During the course of this investigation Amberlite IR-120 was utilised. Initially the acid form of this resin was employed but the zinc cyanide complex was found to be unstable under the low pH conditions of such a separation and both zinc and magnesium were completely removed from a cyanide solution. Replacement of the hydrogen form of the resin by its sodium counterpart did yield almost complete separation of the two metals.

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*Demasking of zinc cyanide complex by formaldehyde**

After this separation of the complex zinc cyanide from the magnesium, it was required to liberate free zinc ions from the complex in order to apply the volumetric finish using Complexone III. FEIGL[7,8] used formaldehyde in similar circumstances to demask nickel, cadmium and copper before application of various reactions, the mechanism of the reaction being the formation of a salt of glycolic nitrile. Recently KINNUNEN AND MERIKANTO[9] used a similar technique to demask zinc ions in the presence of copper before complexometric titration of the zinc. These authors found that simple addition of excess formaldehyde was sufficient to decompose the zinc cyanide complex, and to allow subsequent quantitative determination of the zinc. However, a large excess of cyanide was not employed and the solution was ten times more concentrated than that employed in our procedure. In this case we found that the reaction using formaldehyde did not proceed readily at room temperature but was rapid at boiling point, especially in acid medium. After demasking, it was found possible to obtain quantitative recoveries of zinc by titration with Complexone III at pH 6.8. A correction blank was necessary for very precise results; this blank is mainly attributable to the potassium cyanide and is usually of the order of 0.1 ml of 0.01*M* Complexone III.

Results for the determination of zinc after demasking and also after passage of such complex cyanide solutions through the cation exchanger are given in Table II.

TABLE II

TITRATION OF ZINC AFTER DEMASKING THE CYANIDE COMPLEX WITH FORMALDEHYDE

Zn^{+2} present mg	Zn^{+2} found mg	Remarks
3.27	3.28	—
6.54	6.55	—
16.37	16.39	—
26.15	26.16	—
16.37	16.37	Solution passed through Amberlite IR-120 resin
16.37	16.39	

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* After the completion of this investigation, a paper by H. FLASCHKA was published (*Z. anal. Chem.*, 138 (1953) 332). This research describes the demasking of complex zinc and cadmium cyanides by formaldehyde and subsequent complexometric determination of the free ions, the method being applicable in the presence of nickel, mercury, cobalt and copper.

Determination of zinc in presence of magnesium

Attention was now paid to the separation of zinc from magnesium. Separation by the resin was not found to be completely quantitative, as a small amount of magnesium always found its way into the effluent from the column. This, however, was of no consequence, as the zinc was ultimately titrated at pH 6.8, where traces of magnesium did not interfere[1]. Consequently, the solution for analysis may be run through the column at a fast rate, without the precaution of a slow flow as required in most resin procedures. Magnesium interference due to excessive amounts of the metal was noted to a slight extent at the 4 g level of magnesium sulphate; at the 5 g level the end-point was too indistinct for results to be obtained.

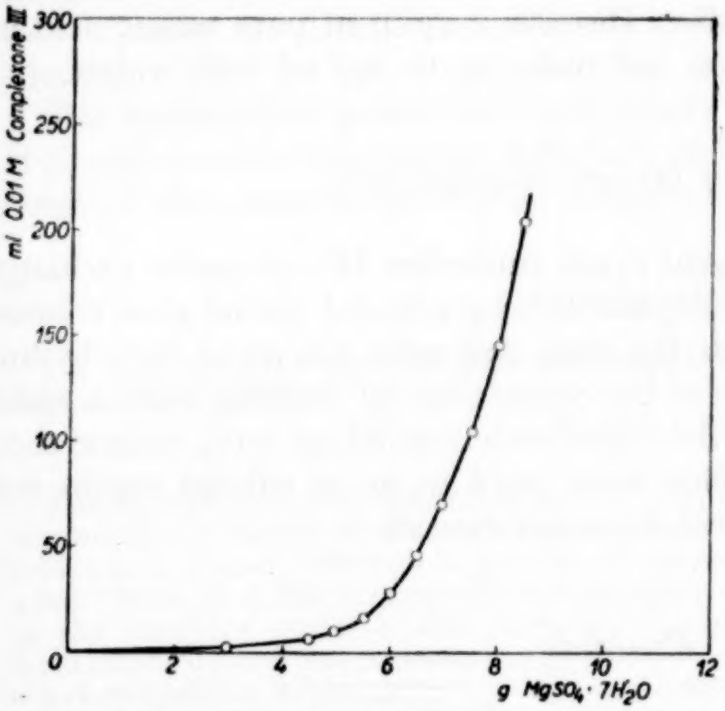

Fig. 1. Breakthrough of $MgSO_4$ using 20 g Amberlite IR-120 resin.

TABLE III

SEPARATION OF ZINC FROM MAGNESIUM SULPHATE BY MEANS OF AMBERLITE IR-120

$MgSO_4.7H_2O$ g	Molecular ratio of Mg:Zn	mg Zn^{+2} present	mg Zn^{+2} found
0	—	16.35	16.35
1	16.2	16.35	16.37
2	32.4	16.35	16.38
3	48.6	16.35	16.34
3	48.6	16.35	16.36
4	64.8	16.35	16.44

The breakthrough of magnesium ions using 20 g of the sodium form of Amberlite IR-120 is graphically represented in Fig. 1 and the results obtained for the separation of zinc from varying quantities of magnesium sulphate are given in Table III. A complete analysis takes about 45 minutes.

METHOD

Reagents

0.01*M* Complexone III solution. Dissolve 3.722 g of B.D.H. disodium dihydrogen-ethylenediamine tetra-acetate dihydrate in one litre of water, preferably redistilled. Standardize against 0.01M zinc solution prepared from pure metallic zinc.

2.5% w/v Potassium Cyanide Solution. Prepared from the analytical reagent grade material.

4% v/v Formaldehyde Solution. Prepared from 40% AnalaR reagent.

Approximately N Hydrochloric Acid Solution.

Approximately N Sodium Hydroxide Solution.

0.1% w/v Bromothymol Blue.

0.5% w/v Solochrome Black W.D.F.A. Dissolve 0.5 g Solochrome Black W.D.F.A. in a mixture of 50 ml triethanolamine and 50 ml *iso*propanol[1]. This indicator solution is stable for three months.

Maleic Acid-Sodium Maleate Buffer. Dissolve 2.436 g of pure maleic acid in 40 ml N sodium hydroxide solution and make up to 200 ml with water.

Preparation of the ion exchange resin

Introduce 20 g of analytical reagent grade Amberlite IR-120 cation exchange resin into a suitable column. In these experiments a graduated 100 ml glass column fitted with a tap was used. Wash the resin first with 100 ml of 10% hydrochloric acid solution. Remove most of the excess acid by washing with a small quantity of water. Again wash the resin with 100 ml of 10% caustic soda solution and then wash with distilled water until 50 ml of effluent require less than 0.1 ml of 0.1N hydrochloric acid for neutralization.

Procedure

To the solution of magnesium and zinc salts containing less than 4 g $MgSO_4.7H_2O$ and sufficient zinc to obtain a suitable titration value add 10 ml of 2.5% potassium cyanide solution. Neutralize if necessary and make just alkaline to bromothymol blue. Pass the solution so obtained through the prepared column at between 3 to 5 ml per minute, collecting the effluent in a 500 ml-flask. Wash the beaker with several small portions of distilled water and add these washings to the solution in the column. Finally, wash the column with approximately 100 ml of distilled water. Make the effluent solution from the column acid to bromothymol blue by adding 5 ml N hydrochloric acid in excess of that required for neutralization. Add 10 ml 4% formaldehyde solution and heat to incipient boiling. If the solution becomes blue and a precipitate forms, insufficient acid has been added. Cool the solution and carefully neutralize with caustic soda solution. Add 20 ml of the maleic acid-maleate buffer and 5-6 drops of the Solochrome indicator solution. Titrate to the first sharp change from violet-red to blue-grey.

DISCUSSION OF THE METHOD

The procedure described using an ion exchange method of separation proved more effective than conventional chemical means. Attempts at precipitating the magnesium as hydroxide from cyanide solutions of zinc and magnesium showed that considerable coprecipitation also occurred. The ion exchange method also provides a possible means of separating zinc from those metals not forming stable cyanide complexes. Metals forming complex cyanides which are not demasked by formaldehyde, for example, copper, are without effect[7].

The method of regenerating the column in two stages gave more consistent results than a single regeneration using sodium chloride solution. No critical study of this effect was made, as the use of caustic soda had the added advantage that it made the detection of the efficiency of washing easier and hence was adopted.

This method then provides a ready means of determining zinc in the presence of a large excess of magnesium without a preliminary separation and extends the range of the previous differential procedure[1].

ACKNOWLEDGEMENTS

We wish to thank the Directors of British Enka Limited, for permission to publish this communication.

SUMMARY

The complexometric determination of zinc in the presence of large quantities of magnesium is described. Zinc is converted into the complex cyanide and the resultant solution is passed through a column of cation-exchange resin (Amberlite IR-120) when the bulk of the magnesium is separated off and the zinc is collected unchanged as the complex cyanide. Zinc ions are liberated from the complex by means of formaldehyde and are subsequently titrated at pH 6.8 with disodium dihydrogen ethylenediamine tetra-acetate solution (Complexone III).

RÉSUMÉ

Une détermination complexométrique du zinc, en présence de grandes quantités de magnésium, est décrite. Le zinc est converti en complexe cyané, puis il est séparé du magnésium au moyen de l'échangeur d'ions Amberlite IR-120. Les ions zinc sont libérés du complexe par le formaldéhyde et dosés ensuite par une solution d'éthylènediaminotétracétate disodique (complexon III), au pH 6.8.

ZUSAMMENFASSUNG

Es wird die komplexometrische Bestimmung von Zink in Gegenwart grosser Mengen Magnesium beschrieben. Zink wird in den Cyankomplex übergeführt und die entstehende Lösung wird durch eine Säule des Kationaustauscher Harzes Amberlite IR-120 durchlaufen lassen, wodurch der Hauptteil des Magnesiums abgetrennt wird and das Zink als Cyankomplex unverändert hindurch geht. Die Zinkionen werden durch Zusatz von Ameisenaldehyd aus dem Cyankomplex in Freiheit gesetzt und werden anschliessend bei pH 6.8 mit Dinatrium-Äthylendiamin-Tetraacetat-Lösung (Komplexone III) titriert.

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DOSAGE COLORIMÉTRIQUE DE FAIBLES QUANTITÉS DE CÉRIUM DANS L'URANIUM

par

J. HURÉ ET MME R. SAINT JAMES-SCHONBERG

Département de métallurgie et chimie appliquée, Section de Recherches analytiques, Commissariat à l'énergie atomique, Saclay (France)

Le problème posé était le dosage de quantités de cérium comprises entre 0 et 100 ppm dans les uranates. Les impuretés possibles sont: fer, manganèse, chrome, vanadium, nickel, cuivre, aluminium.

PRINCIPE DU DOSAGE

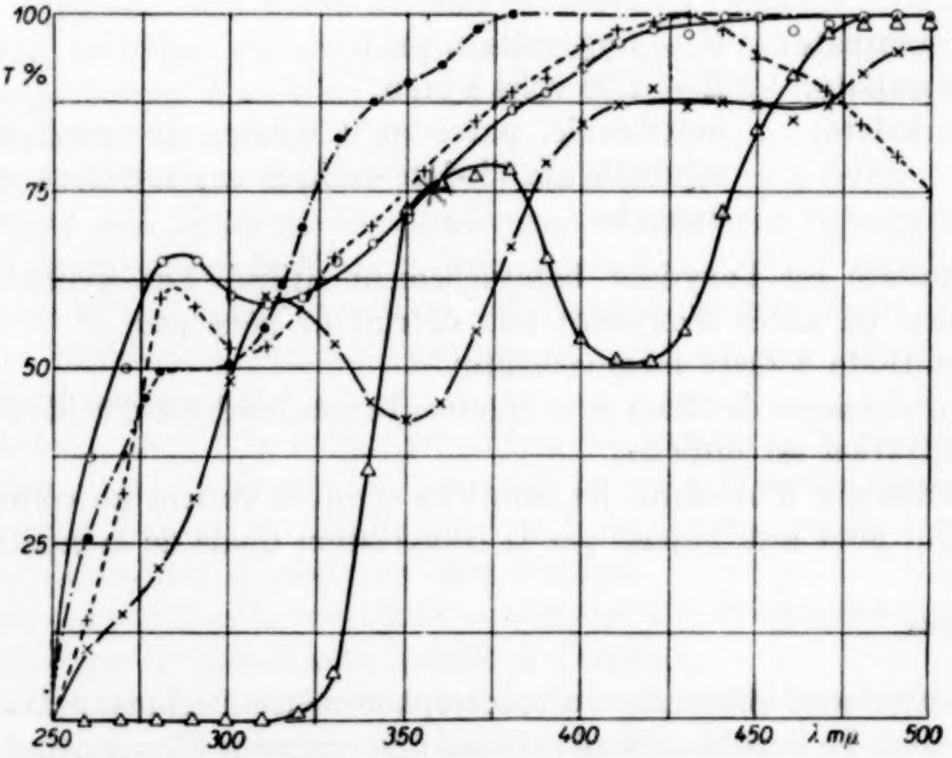

Fig. 1. Courbes de transmission:
—o— Ce^{+4}; —×— Cr^{+6}; —Δ— UO_2^{+2}; —+— MnO_4^-; —·—·— V^{+5}

Nous utilisons l'absorption des radiations ultra-violettes par l'ion cérique. En examinant les courbes de transmission dans l'ultra-violet pour les principaux constituants de la solution (Fig. 1), on constate que pour l'ion cérique, l'absorption

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présente un maximum entre 300 et 320 millimicrons. Cependant, si l'on utilise cette longueur d'onde, l'absorption par l'uranium est considérable. Il vaut donc mieux perdre en sensibilité et opérer aux environs de 360 millimicrons où l'influence de petites quantités d'uranium devient négligeable.

A cette longueur d'onde, on ne peut négliger l'action du vanadium, du chrome, et du manganèse. L'absorption due à ce dernier peut être évaluée par une mesure à une autre longueur d'onde. Pour éliminer l'influence des deux premiers, il suffit de tarer le spectrophotomètre sur une solution identique à la solution de mesure, mais où on aura effectué préalablement une réduction sélective du cérium et du manganèse.

Il ne reste à éliminer que le fer et la majeure partie de l'uranium.

CHOIX DE L'OXYDANT

On mesure l'absorption due aux ions cériques en milieu sulfurique normal[1]. Il faut donc oxyder la solution pour amener le cérium à l'état cérique.

Dans les conditions d'opération, le potentiel d'oxydo-réduction du cérium est de 1.44 volts.

Trois oxydants sont théoriquement possibles:

a) le bismuthate: $E = 1.73$ volts à pH 0
b) le persulfate: $E = 1.80$ volts à pH 0
c) le periodate: inutilisable, parce qu'il donne, en raison de la faible solubilité de l'iodate cérique des solutions oxydées très instables.

Le persulfate est l'oxydant habituellement utilisé. Les solutions obtenues sont stables, un excès d'oxydant non détruit ne gêne pas.

Le bismuthate a deux inconvénients:

a) Il est nécessaire de filtrer pour éliminer l'excès insoluble d'acide bismuthique, et cette filtration est difficile;

b) En l'absence d'oxydant, les solutions cériques varient au cours du temps.

L'oxydant nous sera imposé par la composition finale de la solution à doser.

Ions gênants

Les mesures sont effectuées au spectrophotomètre Beckmann D. U avec des cuves en silice. Le liquide mesuré est sous une épaisseur d'un centimètre (voir les figures no 1).

Uranium: 1 milligramme d'uranium par centimètre cube absorbe toute la lumière à 310 millimicrons. 0.2 milligramme d'uranium par centimètre cube seront tolérables à condition d'effectuer les mesures à 360 millimicrons, ce qui diminue de moitié la sensibilité du dosage. La densité optique d'une solution à 0.2 mg d'uranium par ml est de 0.100.

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Fer: Le fer absorbe fortement dans l'ultra-violet. Au-delà de 0.5 mg de fer par ml, il devient impossible de tarer le spectrophotomètre.
Manganèse: La loi de BEER étant valable à 525 et à 360 millimicrons, il est possible par une mesure à 525 millimicrons, où seul MnO_4^- absorbe, d'évaluer l'absorption de cet ion à 360 millimicrons.
Chrome: Le bichromate absorbe lui aussi dans l'ultra-violet. Comme expliqué précédemment, le choix d'un réducteur sélectif doit permettre de n'en pas tenir compte.
Vanadium: Même observation.
Acide phosphorique: Le phosphate cérique est peu soluble. En milieu très acide, il existe un complexe cériphosphorique qui diminue la sensibilité déjà faible de la coloration. Les phosphates sont donc à éviter.
Ions nitriques: Les ions nitriques ne gènent pas.

CHOIX D'UN RÉDUCTEUR SÉLECTIF

La réduction sélective citée plus haut nécessite un réducteur dont le potentiel d'oxydo-réduction soit compris entre ceux du cérium et du manganèse d'une part, du bichromate et du vanadate d'autre part.

Nous pouvons utiliser trois réducteurs.

a) l'eau oxygénée: elle donne de bons résultats en l'absence de chrome, mais CrO_4^{-2} forme, en milieu sulfurique, un complexe avec l'eau oxygénée dont l'absorption est inférieure à celle du bichromate. Il en résulte une erreur par excès dans l'évaluation du cérium.

b) l'azoture de sodium: il ne réduit que le manganèse et le cérium (IV). Néanmoins, il forme avec le fer un complexe rouge orangé dont l'absorption est très faible. La tolérance pour le fer se trouve ramenée à 1 ou 2 mg dans 20 ml. Si l'oxydation se fait par le persulfate, catalysée par les ions argent, l'azoture de sodium sera inutilisable puisque l'azoture d'argent est peu soluble et parfois même explosif en solution.

c) l'acide oxalique: il a les mêmes propriétés que l'azoture. De plus, il complexe le fer et réduit ainsi la tolérance à 1 gamma de fer par centimètre cube. Le chrome gène aussi, mais l'erreur, introduite par 170 γ de chrome, est de l'ordre de 7% pour 100 γ de cérium et elle peut être négligée.

On pourra donc utiliser le persulfate associé soit à l'eau oxygénée, soit à l'acide oxalique; ou bien le bismuthate associé à l'azoture.

Dans tous les cas, il faudra se débarrasser de la plus grande partie de l'uranium et de la presque totalité, soit du fer, soit du chrome, suivant le couple oxydant-réducteur utilisé.

SÉPARATION

1) — On peut essayer d'isoler le cérium par précipitation de l'iodate cérique en présence de thorium entraîneur[2]. La séparation est quantitative; nous l'avons vérifiée par des essais en présence de cérium (III) radio-actif. Malheureusement,

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la redissolution du précipité est difficile, il nous a donc semblé préférable d'utiliser des séparations par solvants.

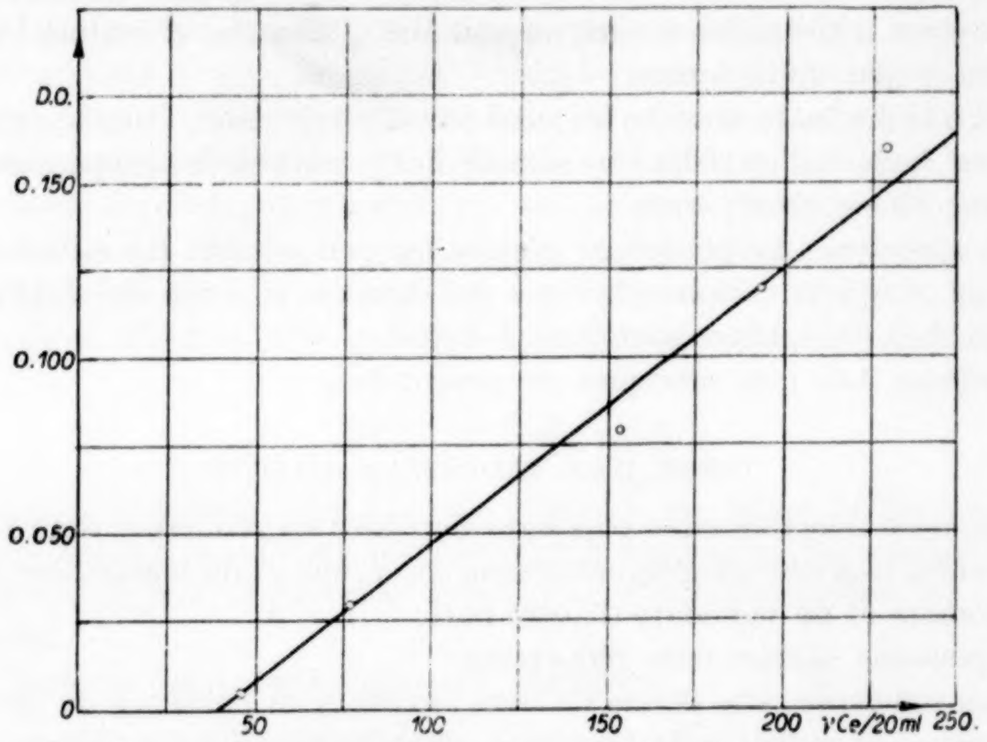

Fig. 2. Colorimétrie Ce^{+4}; oxydation bismuthique.

2) — D'après le rapport de Warf[3], le cérium (IV) est extrait d'une solution nitrique par le tributylphosphate, en même temps que l'uranium. On peut ensuite récupérer le cérium (III) seul par agitation de la phase organique avec une solution d'eau oxygénée. Cependant, ce procédé, applicable à de fortes concentrations en cérium, exige de grandes précautions pour l'extraction de traces. Le solvant brut contient des impuretés réductrices qui gênent l'extraction, en faisant passer une partie du cérium à la valence III. Le dosage de traces exige donc une purification soignée du tributylphosphate.

3) — L'extraction des thiocyanates métalliques par des solvants organiques a été plusieurs fois signalée[4,5].

Nous avons fait plusieurs essais qualificatifs, en vérifiant à chaque fois à l'aide de traceurs, que le cérium (III) restait dans la phase aqueuse.

Les solvants organiques les plus efficaces nous ont paru être le tributylphosphate, même non purifié, la méthyl-*iso*butylcétone, l'acétate d'éthyle.

Le premier cité est nettement le meilleur, mais nous n'en disposions que de faibles quantités et nous ne l'avons pas utilisé pour les dosages en série.

La méthyl-*iso*butylcétone a un coefficient d'extraction légèrement supérieur à celui de l'acétate d'éthyle pour l'uranium, inférieur pour le fer.

En raison de la faible tolérance du dosage pour le fer, nous avons préféré ce dernier solvant.

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CONDITIONS DE L'EXTRACTION

L'acide thiocyanique n'est pas un acide très fort, on n'a donc pas intérêt à opérer en milieu très acide. Les solutions étaient normales ou demi-normales en acide nitrique, ce qui est conforme aux indications de BOCK[5]. La quantité de thiocyanate optima est comprise entre 10 et 15 moles de thiocyanate par mole de fer ou d'uranium. Un excès de thiocyanate gêne l'extraction. D'après BOCK[5], il se formerait des complexes supérieurs difficilement extractibles.

Dans le cas de l'acétate d'éthyle, ayant au départ 10 centimètres cubes d'une solution contenant 800 milligrammes d'uranium, 2.5 grammes de thiocyanate, et demi-normale en acide nitrique, après 4 extractions, à volume égal, nous arrivons à une teneur de 150 γ en uranium.

$$\frac{C_4}{C_0} = \frac{150}{800{,}000} = 1.9 \cdot 10^{-4} = \frac{1}{(1+K)^4}\,;$$

$$1 + K = \frac{1}{\sqrt[4]{1.9 \cdot 10^{-4}}} = 8.5$$

Ceci n'est qu'un calcul approché, relatif à un pourcentage d'extraction global, les conditions des 4 extractions n'étant pas identiques (l'acide thiocyanique est extrait par l'acétate). Il donne une idée de l'efficacité de l'acétate d'éthyle.

Remarque

Le thiocyanate réduit le cérium (IV); il est donc nécessaire de l'éliminer.

La phase aqueuse est amenée à sec, reprise par l'acide nitrique concentré qui oxyde le thiocyanate et par quelques gouttes de brome qui facilite l'oxydation du soufre formé.

OXYDATION

Il ne reste maintenant en solution que le cérium initial, environ 200 γ par centimètre cube d'uranium, et des traces des autres composés.

Pour arriver à des quantités de fer non gênantes, il faudrait un certain nombre d'extractions. Nous avons tenté de mettre au point la colorimétrie après oxydation par l'acide bismuthique, qui — comme nous l'avons vu — permet de tolérer de plus fortes quantités de fer; la solution servant à tarer le spectrophotomètre est dans ce cas réduite par l'azoture de sodium. Les figures 2 et 4 indiquent clairement les inconvénients de ce procédé, on peut néanmoins obtenir des résultats cohérents, à condition d'effectuer les mesures immédiatement après filtration.

Il est préférable, cependant, d'oxyder la solution par le persulfate, après quatre extractions par l'acétate d'éthyle. Le fer est en suffisamment faibles quantités pour donner une erreur acceptable. On réduira une aliquote de la solution par l'acide oxalique pour effectuer le tarage du spectrophotomètre.

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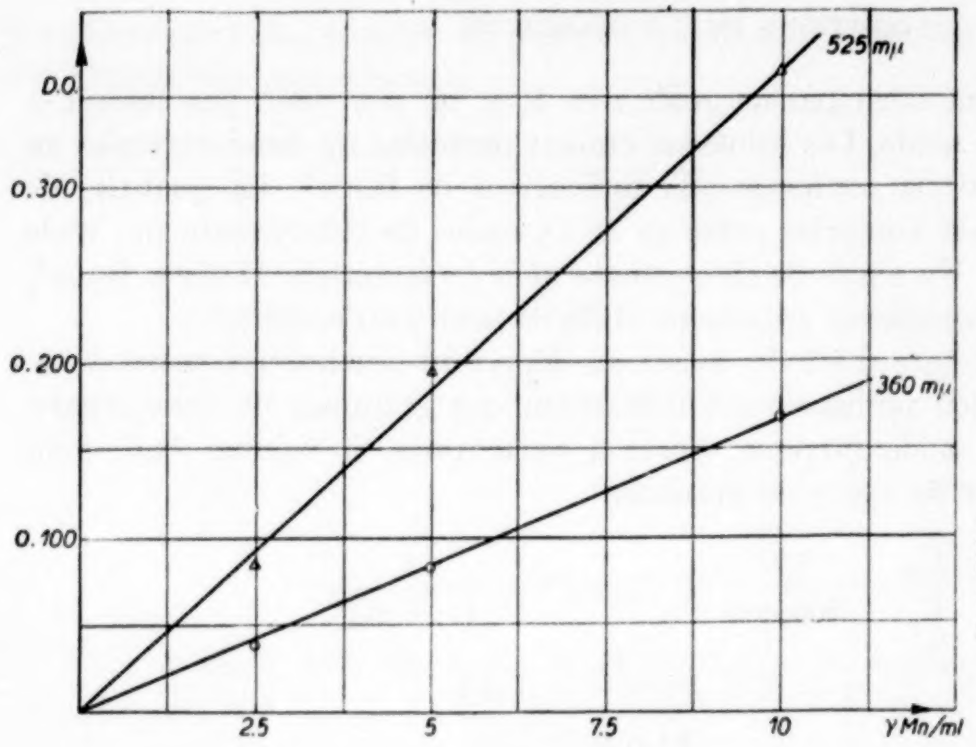

Fig. 3. Mn oxydation bismuthique; blanc: 10 ml sol. + 5 g azide 10%.

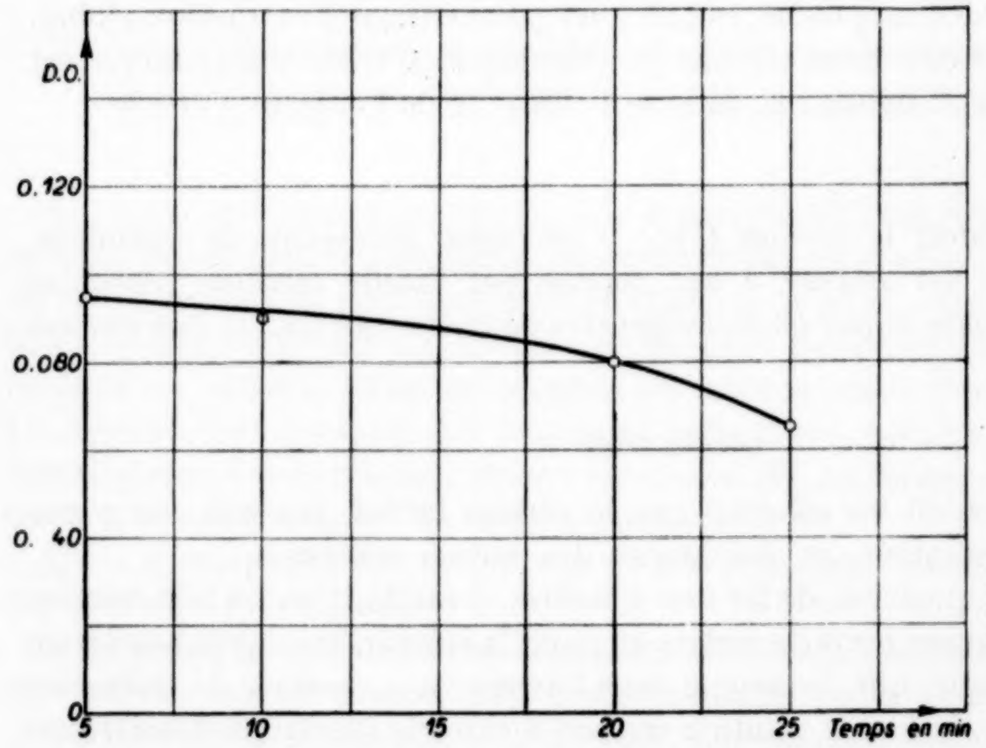

Fig. 4. Densité optique en fonction du temps.

MODE OPÉRATOIRE

Réactifs

Dissoudre dans l'acide nitrique des quantités d'uranate suffisantes pour obtenir une concentration finale d'environ 100 milligrammes d'uranium par centimètre cube et moléculaire en H^+.

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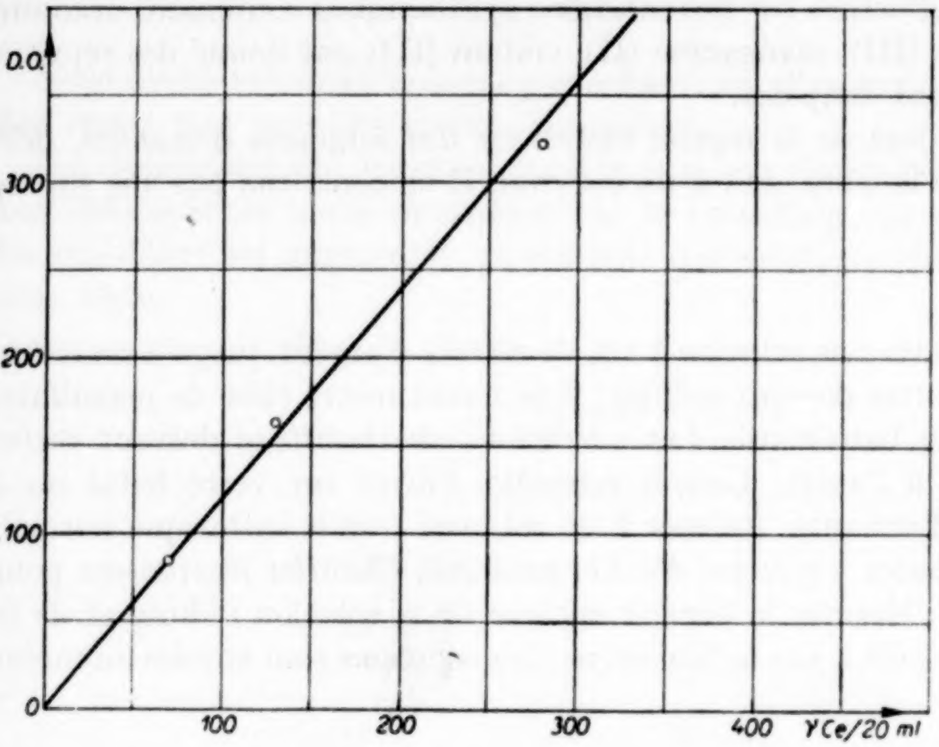

Fig. 5. Colorimétrie Ce^{+4}; oxydation par le persulfate.

L'acétate d'éthyle utilisé est l'acétate commercial pur, non redistillé. Cet acétate est, préalablement à l'extraction, saturé d'eau.

L'oxydant est une solution à 10% de persulfate d'ammonium.

Le réducteur est une solution d'acide oxalique à 2%.

La moindre impureté organique réduit le cérium: l'eau qui servira à préparer l'acide sulfurique normal, est préalablement oxydée par le bismuthate; les cuves, fioles, frittés, amiante, sont lavés avec du permanganate et rincés avec un peu d'acide nitrique ou sulfurique.

Extractions

10 ml de la solution d'uranate sont additionnés de 2 g de thiocyanate d'ammonium et agités avec 10 ml de solvant. Trois à quatre extractions sont nécessaires. Il est utile d'acidifier légèrement la solution après la seconde extraction, pour éviter toute précipitation dans la phase aqueuse et d'ajouter un peu de thiocyanate (400 à 500 mg).

Les phases organiques ne sont pas relavées: l'erreur due à la quantité de fer et d'uranium qui repasse en phase aqueuse a été jugée supérieure à celle que l'on commet en négligeant le cérium entraîné dans le solvant. On sépare les deux phases en siphonnant le solvant, ce qui réduit considérablement les risques d'entraînement du cérium.

La phase aqueuse est amenée à sec, reprise avec précaution par 1 ml d'acide nitrique concentré; laisser réagir, ajouter alors quelques gouttes de brome. Amener à sec, recommencer l'opération si nécessaire. Reprendre finalement par 10 ml d'acide sulfurique normal.

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N.B. Tous les essais effectués sur des solutions synthétiques contenant uranium (VI), fer (III), chrome (III), manganèse (II), cérium (III) ont donné des reprises sulfuriques parfaitement limpides.

Le trouble observé lors de la reprise sulfurique des solutions d'uranate, doit être attribué soit à de la silice, soit à du baryum. Il ne constitue pas une source d'erreur.

Oxydation

Ajouter goutte à goutte une solution à 1% de nitrate d'argent, jusqu'à cessation de précipité (3 à 4 gouttes doivent suffire); puis 1 centimètre cube de persulfate. Laisser 15 minutes au bain-marie. Les conditions de chauffage doivent rester identiques d'un essai à l'autre. Laisser refroidir. Filtrer sur verre fritté no 4 recouvert de bourre d'amiante. Amener à 20 ml avec l'acide sulfurique normal.

Prélever 10 ml. Ajouter 5 gouttes d'acide oxalique. Chauffer légèrement pour accélérer la réduction. Mesurer la densité optique de la solution réduite et de la solution oxydée à 360, puis à 525 millimicrons. Les solutions sont stables au moins 1 heure.

Étalonnage

La solution étalon de cérium est préparée par dilution d'une solution de sulfate céri-ammonique $0.01N$ dosée volumétriquement par le sel de MOHR.

Le coefficient d'absorption K, défini par la loi de BEER:

$$\mathrm{D.O} = K.l.c.$$

(D.O est la densité optique; l est l'épaisseur de la solution: dans ce cas 1 cm; c est la concentration exprimée en γ par ml), vaut ici:

$$K = \frac{230}{10} = 23$$

Le rapport des densités optiques qui traduit l'absorption par le permanganate à 525 et 360 millimicrons est de:

$$\frac{\mathrm{D.O}_{360}}{\mathrm{D.O}_{525}} = 0.45 \qquad (cf. \text{ Fig. } 3)$$

Précision

L'erreur relative n'excède pas 15% pour les faibles quantités de cérium, 20 à 50 ppm. En l'absence de chrome, elle peut devenir inférieure à 5%.

Limite de sensibilité

La coloration de l'ion cérique est assez faible. On peut détecter 1 γ/ml soit, dans les conditions opératoires indiquées, 20 ppm dans l'uranium. La densité optique pour 20 γ dans 20 ml est de 0.025.

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RÉSULTATS

Nous avons fait deux dosages par échantillon d'uranate, en ajoutant dans l'un des essais une quantité connue de cérium.

Des dosages ont été effectués après la mise au point de l'oxydation bismuthique. Les colorimétries après oxydation par le persulfate ont confirmé les résultats. La sensibilité est augmentée, la stabilité des solutions plus grande, la filtration plus aisée.

No. de l'échantillon	Densité optique après déduction Mn	Ce trouvé
5	88	72
5 + 139 γCe	247	206
10	83	78
10 + 154 γCe	287	240
12	80	66
12 + 139 γCe	240	200
13	73	60
13 + 154 γCe	257	214

Cette méthode de dosage ne donne qu'une précision médiocre, suffisante toutefois dans le problème considéré. Dans ces conditions le dosage est simple, relativement rapide, et utilisable pour des opérations en série.

RÉSUMÉ

La solution à doser, après extraction des thiocyanates de fer et d'uranium par l'acétate d'éthyle, est oxydée par le persulfate d'ammonium (en présence de nitrate d'argent). L'absorption de cette solution est mesurée à 360 millimicrons par rapport à celle d'une partie aliquote préalablement réduite par l'acide oxalique, qui amène sélectivement le cérium et le manganèse aux valences inférieures. L'absorption due au manganèse est déduite d'une mesure à 525 millimicrons. On détermine ainsi 1 à 5 γ/ml de cérium avec une erreur inférieure à 15%.

SUMMARY

After extraction of the iron and uranium thiocyanates by ethyl acetate, the solution is oxidised by ammonium persulphate (in the presence of silver nitrate). The absorption of this solution is measured at 360 mμ by comparison with that of an aliquot previously reduced with oxalic acid, which selectively reduces cerium and manganese to the low valences. The absorption of manganese is deduced from a measurement at 525 mμ. By this method 1 to 5 γ/ml cerium can be determined with an error of less than 15%.

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ZUSAMMENFASSUNG

Nach der Extraktion des Eisen- und Uranthiocyanats mit Äthylacetat wird die zu bestimmende Lösung durch Ammoniumpersulfat in Gegenwart von Silbernitrat oxydiert. Die Absorption dieser Lösung wird zu 360 millimicron bestimmt, unter Berücksichtigung der Absorption eines aliquoten, vorher mit Oxalsäure (die Cer und Mangan vollständig in die niedrigeren Wertigkeitsstufen überführt) reduzierten Teiles. Die dem Mangan zuzuschreibende Absorption wird aus einem Wert von 525 millimicron abgeleitet. Man kann so 1 bis 5 γ/ml Cer mit einem Fehler, der geringer als 15% ist, bestimmen.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE

III. THE REACTION MECHANISM OF THE ALUMINIUM-HAEMATOXYLIN REAGENT

by

B. J. MacNULTY and G. J. HUNTER

Chemical Inspectorate, Ministry of Supply, Kidbrooke, London, S.E. 3 (England)

INTRODUCTION

A method has been developed recently[1, 2] in which fluoride is determined by its effect on the complex between aluminium and haematoxylin. This complex is intensely coloured and very sensitive to fluoride. Preliminary experiments indicated that aluminium did not form such complexes with the similar compounds brazilin and haematein. Experiments with dilute solutions with a view to extending the range of the method, the present lower limit of which is about 0.02 p.p.m., showed that the complex was less stable in dilute solution. It was decided therefore to carry out a spectrophotometric study of the method in an attempt to elucidate the reaction mechanisms involved.

Under suitable conditions solutions of haematoxylin give highly coloured complexes with many metals (Al, Fe, Zr, Th, Sn, Ge, etc.)[3] and these compounds have been used for determination of the metal in the cases of aluminium[4, 5] tin[6, 7] and germanium[8]; the zirconium compound has been used to determine mg quantities of fluoride[9, 10].

Haematoxylin is a white crystalline solid which becomes pink in the course of a few days on exposure to the atmosphere. It is readily soluble in hot water from which it may be crystallised satisfactorily provided a small amount of bisulphite is added to the solution to minimise oxidation[11]. The colour of a freshly prepared solution is pale yellow, occasionally almost colourless, but it turns red after several days at room temperature. Haematoxylin has been used as an acid base indicator the red solution becoming red violet at pH values above about 6.5.

Haematoxylin (I) has the formula $C_{16}H_{14}O_6$, and its structure was elucidated by Robinson and his co-workers[12]; it normally possesses three molecules of water of crystallisation.

Haematein (II) is an oxidation product of haematoxylin containing two less hydrogens than the latter and has no water of crystallisation. Its structure was also determined by Robinson[13]. It is not very soluble in water.

Brazilin (III) a closely related compound to haematoxylin differs from it in possessing one less hydroxyl. The structure was determined by ROBINSON[12].

EXPERIMENTAL

Behaviour of haematoxylin solutions

The normal procedure for preparing a solution of haematoxylin is to dissolve the solid in hot water, but since, as indicated by the colour change, an alteration takes place, it was considered that a more reproducible solution would be obtained by dissolving the solid in a little alcohol and making up to volume with cold water. In this manner, using material prepared by recrystallisation from water in the presence of bisulphite, it was found possible to prepare almost colourless solutions of haematoxylin (0.1%). These solutions, however, reacted only very slowly with aluminium to give a complex and had to be aged for at least twenty-four hours before they were suitable for use. During this ageing process the colour of the solutions changed through yellow to a deep red. This change has been followed spectrophotometrically and the absorption curves of a freshly prepared solution and one twenty-four hours old are shown amongst others in Fig. 1.

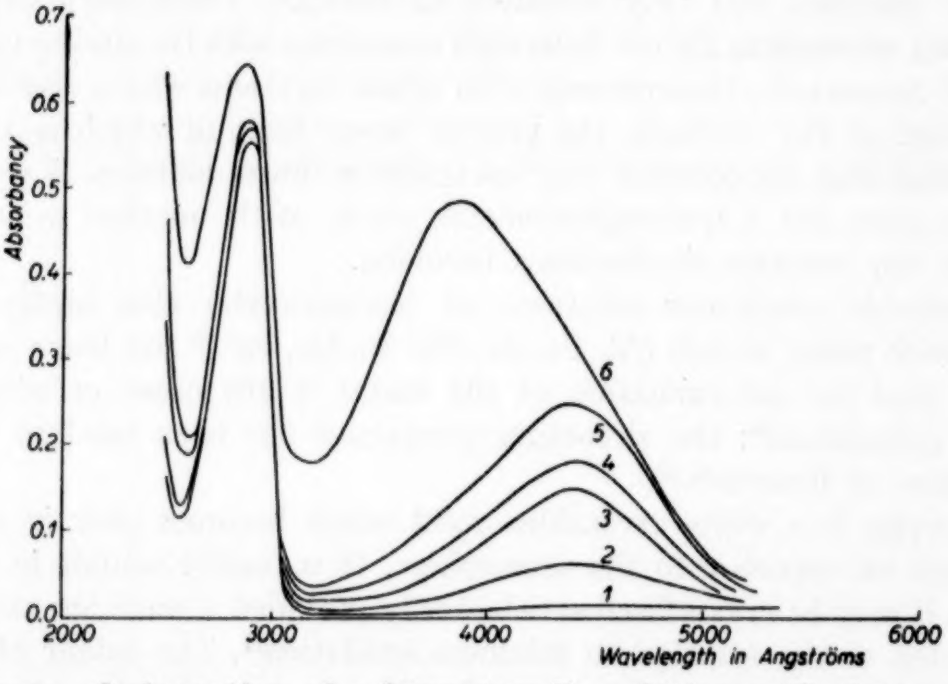

Fig. 1. Change of absorption of a haematoxylin solution with time
Age of solution: 1 1 hour 4 14 days
2 2 days 5 23 days
3 7 days 6 55 days

The rate of formation of the red colour in solutions of haematoxylin was also studied using the absorption peak which appears at 4470 A. The absorbancies of the solutions at various pH values were plotted against time and the initial rate in terms of the extinction at 4470 A found at zero time; the logarithms of

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these rates plotted against pH gave an almost linear relationship. This treatment was carried out between pH values 4.7 and 5.2; above this range the rate was too fast to be conveniently measured spectrophotometrically on the instruments available, and furthermore the indicator colour change begins to become important at pH values greater than 5.3. Results are shown in Table I. It is clear that the rate of formation increases with pH.

TABLE I

Haematoxylin g/litre	pH	Initial rate of formation of red colour *	Temperature °C
0.5	4.97	0.0206	35
1.0	4.97	0.0396	35
2.0	4.97	0.0758	35
1.0	4.7	0.0258	35
1.0	5.21	0.0620	35
1.0	5.29	0.0960	35
1.0	4.97	0.0120	26.5

* Units increase of Absorbancy$_{2}^{601}$ per min.

The behaviour of the haematoxylin solution in dilute acid has been followed spectrophotometrically for long periods and the complete change recorded is shown in Fig. 1. Individual spectra of aged haematoxylin in more dilute acid pH 6.2 and faintly alkaline solution pH 7.2 are shown in Fig. 3a.

Behaviour of haematein solutions

Haematein the first product obtained on mild oxidation of haematoxylin is a brown solid with a silver lustre. It is only sparingly soluble in water or alcohol. The material may be used as an acid-base indicator and the pKa value is about 6.5 as indicated by half neutralisation measurements of pH. The colour change exhibited here is very similar to that shown by an aged solution of haematoxylin. The spectrum in alkaline solution is extremely difficult to obtain since the haematein decomposes rapidly under these conditions probably undergoing further oxidation. Spectra of a freshly prepared solution at pH 6.2 and 7.2 are shown in Fig. 3b.

The decomposition of haematein solutions on exposure to air, which takes place under acid as well as alkaline conditions, being relatively slow in the former rapid in the latter case, has also been studied. The results (Fig. 2) indicate the formation of a substance which we refer to as H_D, the spectrum of which at a pH of about 5 has a peak at 3900 A. In alkali the product H_D itself undergoes oxidation and further products are formed.

The haematein samples used in these experiments were obtained 1) from Hopkins and Williams and 2) by preparation from haematoxylin.

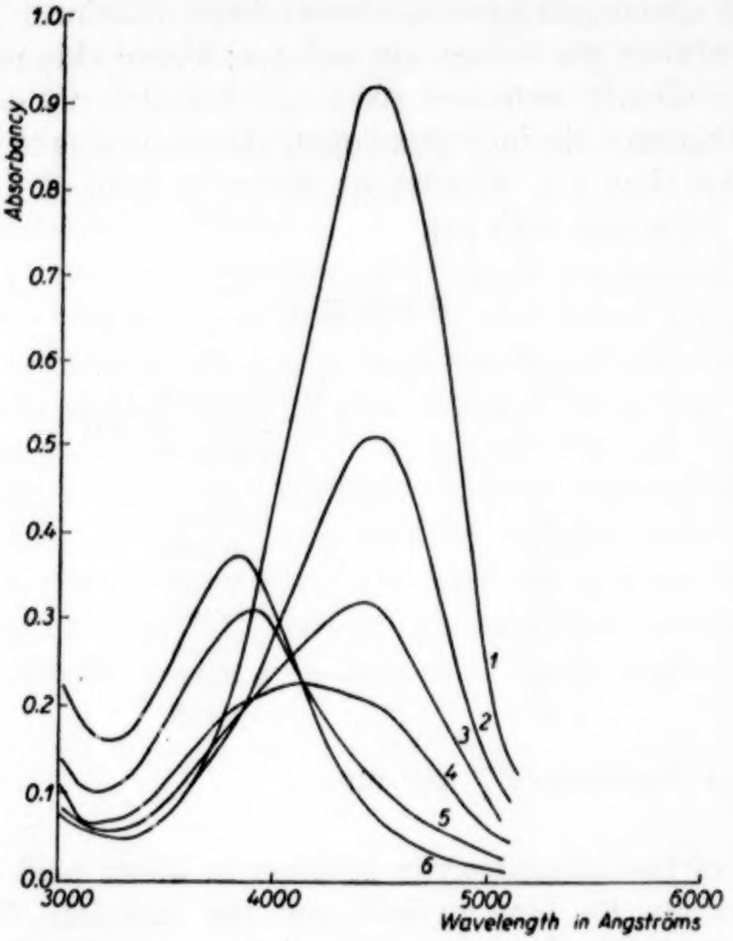
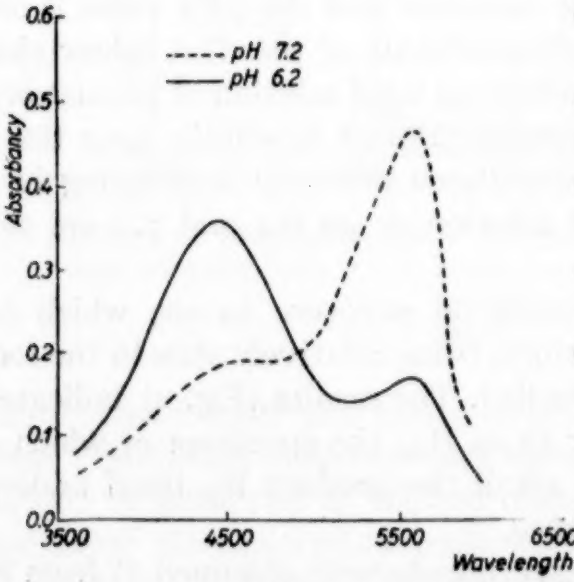


Fig. 2. Change of absorption spectrum of haematein solution with time
Age of solution: 1 freshly prepared 4 4 days
2 1 day 5 14 days
3 2 days 6 38 days



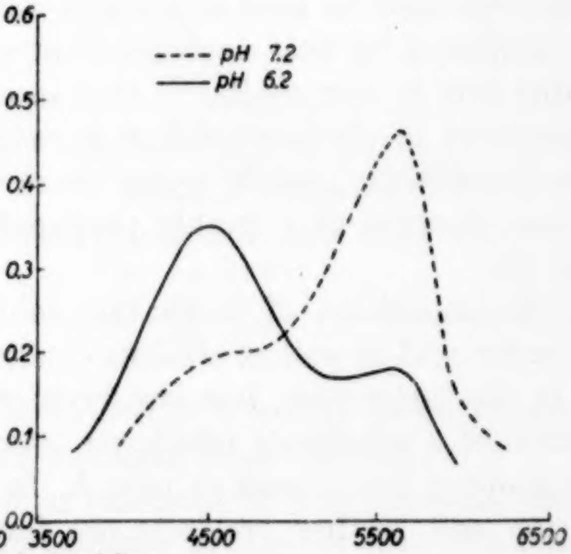


Fig. 3a. Spectra of haematoxylin
Fig. 3b. Spectra of haematein

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Hopkins and Williams haematein. The material appears to contain considerable quantities of haematoxylin and was therefore only used when this fact did not adversely effect the results.

Prepared haematein. Haematein was prepared pure from haematoxylin in the following manner which is similar to ROBINSON's method[13].

3 g solid haematoxylin were added to 30 ml of 1:9 ammonium hydroxide in a large boiling tube. Air, washed with water by sucking through a bubbler, was drawn through the solution, which was cooled by surrounding the vessel with ice, at a rate of between 200 and 250 ml per minute. After six hours the solution was poured in a thin stream into 50 ml of 10% acetic acid, which had been heated on a water bath, and steam was blown into the mixture for 10-15 minutes. The precipitate of lustrous metallic crystals was filtered, washed with water and methanol and allowed to dry overnight.

Behaviour of the aluminium-haematoxylin complex solution

When a solution of an aluminium salt is added to an aged solution of haematoxylin the red colour of the latter is replaced by a deep purple. This applies to solutions which were originally in the pH range 4.2 to 6.0. With solutions below this range no colour change occurs and there appears to be no reaction. Above this range the change is a little less obvious since the haematoxylin under these conditions has some purple colour in it, although this is greatly intensified by the addition of aluminium. Spectrophotometric measurement of the concentration of the material responsible for the red colouration of the haematoxylin solution before the addition of the aluminium and of the concentration of complex formed on addition of aluminium showed a linear relationship between the two, indicating that the complex is formed not by haematoxylin itself but by some material formed from it in solution. Results are quoted in Table II.

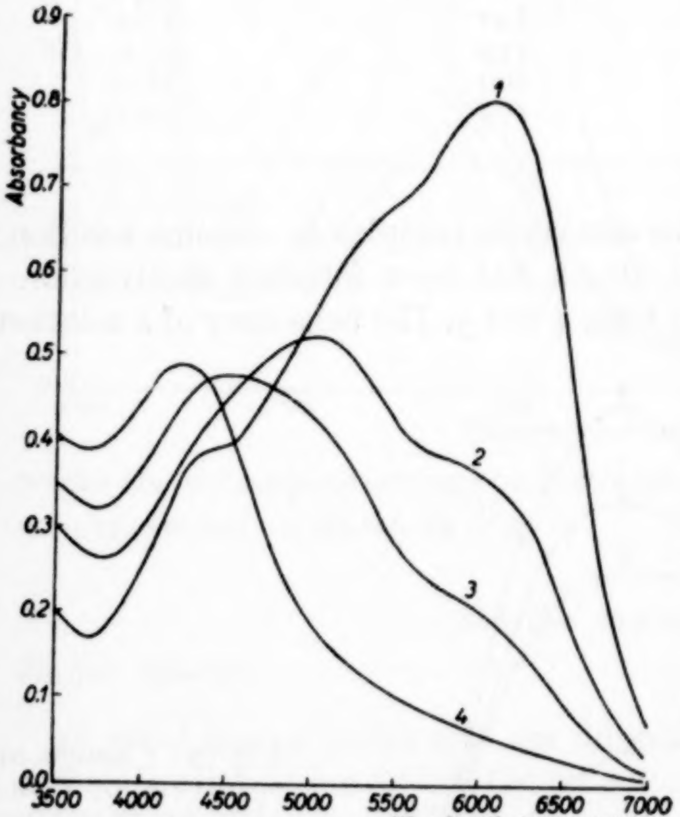

Fig. 4. Change of spectrum of alkaline complex with time

Age of solution: 1 4 hours
2 28 hours
3 2 days
4 7 days

TABLE II

THE CORRELATION BETWEEN RED COLOUR OF SOLUTION (ABSORBANCY AT 4450A) AND AMOUNT OF COMPLEX FORMED WITH ALUMINIUM

Haematoxylin solution 0.1 g/100 ml buffered at pH 4.97 with acetic acid sodium acetate buffer. At intervals 5 ml removed, diluted to 25 ml and absorbancy measured using Ilford 601 filter and a 2 cm cell, this measures amount of red colour formed. At the same time 5 ml of solution were added to 8.88 μg Al and the solution diluted to 25 ml; the amount of complex formed was measured by the absorbancy with an Ilford 606 filter and a 2 cm cell, using a Hilger Spekker absorptiometer.

Time Min	Amount of red colour formed in terms of absorbancy$^{601}_{2} \times 10^3$	Amount of complex formed with aluminium in terms of absorbancy$^{606}_{2} \times 10^3$	Ratio Complex/Red dye as percentage
5	38	14	36.8
21.5	100	39	39
35.25	159	56	35.2
58.5	234	82	35.0
84	294	111	37.4
108.25	340	128	37.6
134	382	144	37.7
160.25	415	155	37.0
182.25	442	169	38.0
191.25	446	175	39.2

The breakdown of the aluminium haematoxylin complex in alkaline solution, and in acid solutions due to fluoride attack has been followed spectrophotometrically and the results are shown in Figs. 4 and 5. The behaviour of a solution

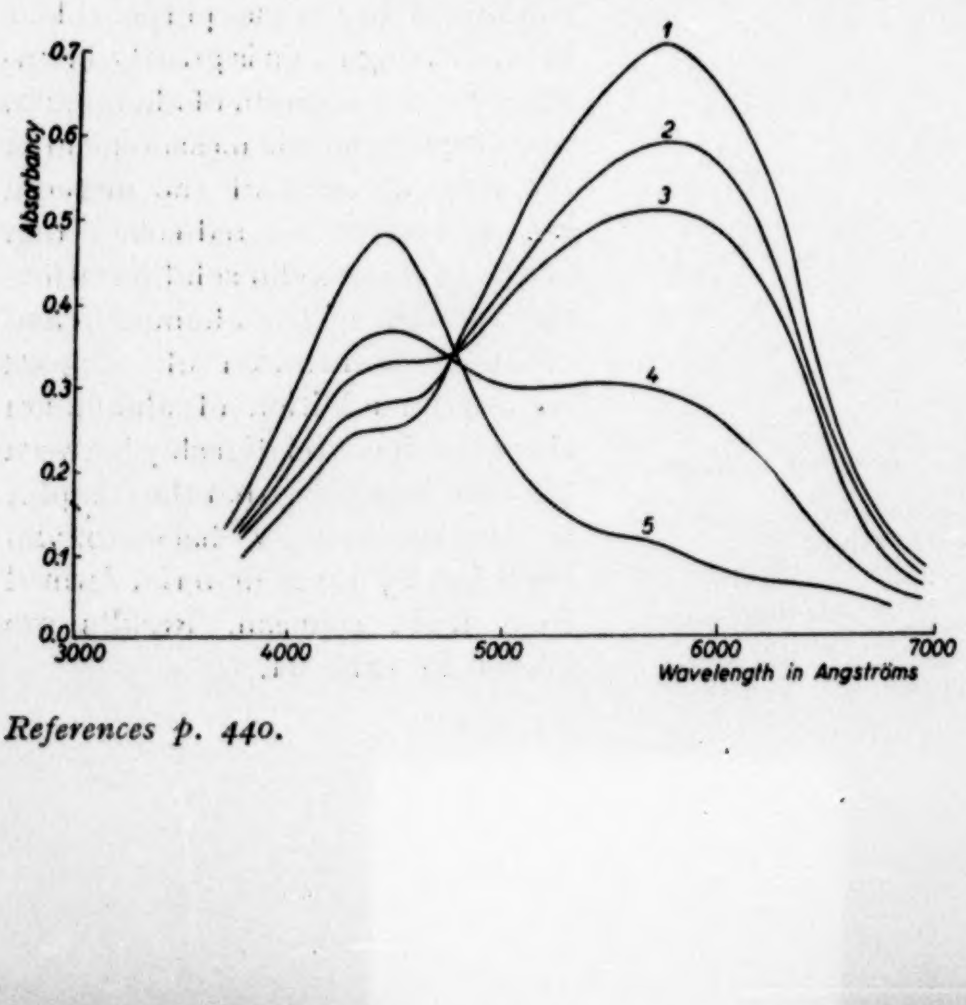

Fig. 5. Change in spectrum of complex produced by fluoride. Original fluoride content:

1 0 μg F^-
2 15 μg F^-
3 25 μg F^-
4 50 μg F^-
5 100 μg F^-

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of complex subsequent to the completion of the fluoride bleaching is shown in Fig. 5a. The pure complex in acid solution (pH 4.9) also breaks down in the absence of fluoride but does so extremely slowly; however, by keeping a solution for some

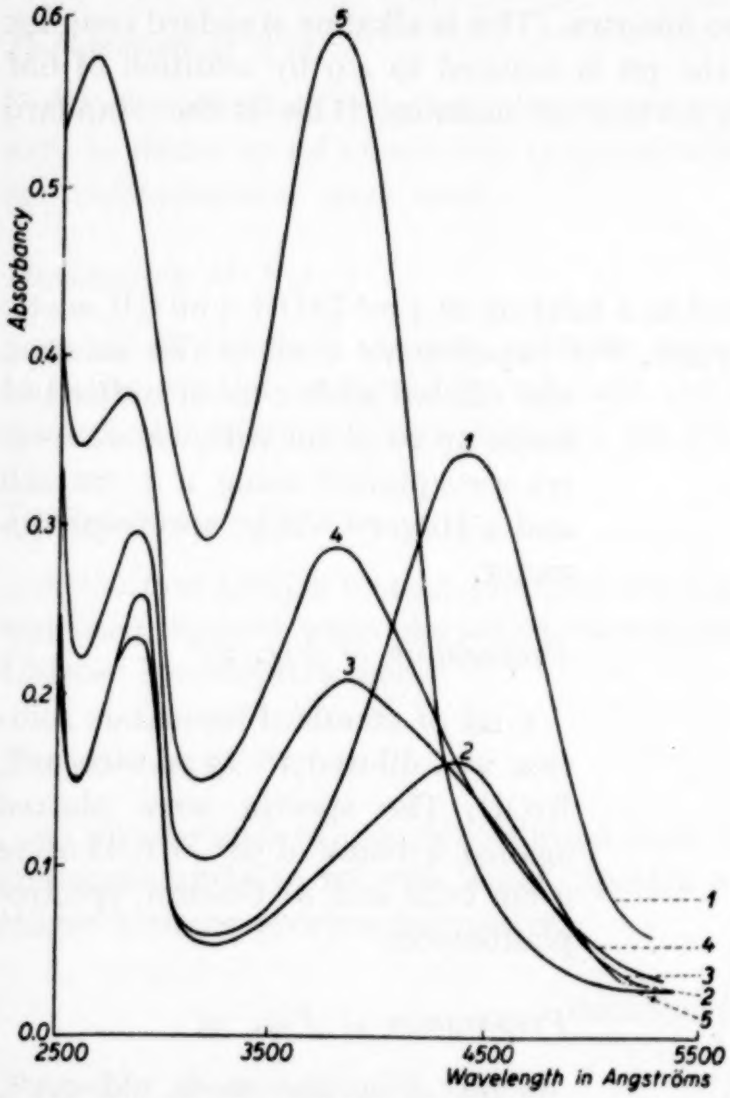

Fig. 5a. Change in absorption spectrum of complex after bleaching by F^-.

Age of solution after fluoride addition:

1	2 hours
2	21 hours
3	92.5 hours
4	187 hours
5	22 days

weeks the decomposition can be followed. The change of spectra recorded in such an experiment is shown in Fig. 6.

Detailed experimental data

Buffer solution

25 ml of glacial acetic acid are diluted to 275 ml with water, 15 ml of 0.880 ammonia solution are added, the pH adjusted to 4.9 with a few drops of ammonia using a pH meter and the volume made up to 300 ml.

Standard haematein solution

5.4 mg of recrystallised haematein were dissolved in a mixture of 25 ml EtOH, 20 ml of water and 2 ml of buffer, and made up to 50 ml with water.

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Standard complex solution

To 250 ml of water were added 1.5 ml gum arabic (5%), 555 μg aluminium, 5 ml 20% ammonium carbonate solution and 10 ml of 0.1% haematoxylin. This solution was allowed to stand 20 minutes. (This is alkaline standard complex solution.) Normally after standing the pH is reduced to 4.9 by addition of 6*M* acetic acid and allowed to stand a further 20 minutes. (This is the standard complex solution.)

Preparation of Fig. 1

0.104 g haematoxylin were dissolved in a mixture of 4 ml EtOH 3 ml 6*M* acetic acid and made up to 50 ml with water. For experiments 1 ml of this solution was diluted with 2 ml of buffer and made up to 50 ml with water. Spectra were plotted using a 1 cm cell and a Hilger Uvispec spectrophotometer.

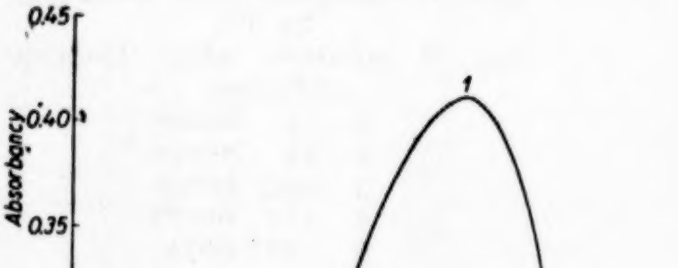

Fig. 6. Change of spectrum of acid complex with time

Age of solution: 1 0 days
2 4 days
3 7 days
4 11 days

Preparation of Fig. 2

1 ml of standard haematein solution was diluted to 25 ml with 50% EtOH. The spectra were plotted against a blank of 50% EtOH using 2 cm cells and a Unicam spectrophotometer.

Preparation of Fig. 3a

2 ml of a one week old 0.1% haematoxylin solution were added to 5 ml of 0.1*M* sodium phosphate and 10 ml of water, the pH was adjusted to 6.2 or 7.2 with 0.1*M* Na OH and the volume made up to 25 ml with water. Spectra plotted using a 2 cm cell and a Hilger Uvispec spectrophotometer.

Preparation of Fig. 3b

1 ml of standard haematein solution was diluted to 40 ml with water, 5 ml sodium phosphate so-

lution (0.1*M*) were added, the pH adjusted to 6.2 or 7.2 by the addition of 0.1*M* caustic soda and the mixture made up to 50 ml with water. Spectra were plotted using a 1 cm cell and a Unicam spectrophotometer.

Preparation of Fig. 4

Alkaline standard complex solution was used. To plot the spectra it was necessary to dilute 20 ml of solution to 50 ml with water. A 1 cm cell and a Unicam spectrophotometer were used.

Preparation of Fig. 5

20 ml of standard complex solution were added to a flask containing 2 ml of buffer solution and *x* μg fluoride and the solution made up to 50 ml. Spectra were plotted after one hour using a 1 cm cell and a Unicam spectrophotometer.

Preparation of Fig. 5a

A solution similar to that prepared for Fig. 5 but containing 300 μg fluoride was used. Spectra were plotted at various times using a 1 cm cell and a Hilger Uvispec spectrophotometer.

Preparation of Fig. 6

10 ml of standard complex solution were diluted with 2 ml of buffer solution and made up to 50 ml with water. Spectra were determined in a 1 cm cell on a Hilger Uvispec spectrophotometer.

DISCUSSION

Behaviour of haematoxylin solution

A fresh solution of haematoxylin possesses an absorption at 2900 A (E_{mol} = 5,500) (Fig. 1) (this form is referred to as H_A) but on ageing a second band appears at 4400-4500 A (this form is referred to as H_B), this peak increases with time and is eventually absorbed into another band appearing at 3850 A (referred to as H_D). In very old haematoxylin solutions (6-12 months) the 4400-4500 A band completely vanishes and the 3950 A band alone remains. Neither freshly prepared (H_A) nor very old haematoxylin (H_D) give a reaction with aluminium. Freshly prepared haematoxylin shows some reaction with aluminium in the presence of alkali, but treatment with alkali leads to the appearance of the 4400-4500 A band when the solution is reacidified. It is clear therefore that the reactive species is not haematoxylin itself but one formed from it.

Although aged haematoxylin does react with aluminium in solutions at pH 4.9 the reaction becomes progressively more rapid as the pH increases; spectra of aged haematoxylin at pH 6.2 and 7.2 (Fig. 3a) indicate that in alkali the species H_B is changed to a form absorbing at 5600 A (H_C) which therefore appears to be the reactive one.

Behaviour of haematein solutions

The spectrophotometric examination of solutions of the closely related haematein revealed that, when freshly prepared, the solution has an absorption peak at 4500 A ($E_{\text{mol}} = 33{,}500$), and that with time the height of this peak falls and the general shape broadens somewhat; eventually it disappears and is replaced by a peak at 3850 A (Fig. 2).

The behaviour is so similar to the later stages of the changes exhibited by haematoxylin solutions that it is concluded that the ageing process of these solutions is in fact the formation of equilibrium amounts of haematein therein.

Investigation of the behaviour of haematein solutions at pH 6.2 and 7.2 (Fig. 3b) in experiments parallel to those with haematoxylin at the same pH values (Fig. 3a), gave identical absorption curves. (In Fig. 3a the peak at 2900 A has been ignored.)

Now the formation of the aluminium complex is more rapid in alkali, conditions which favour the existence of the species of haematein which shows a strong peak at about 5620A. Since the formation of this species is greatly facilitated by alkaline conditions it seems likely that the removal of hydrogen is involved and it is suggested that the essential species in the formation of the complex with aluminium is the haematein ion.

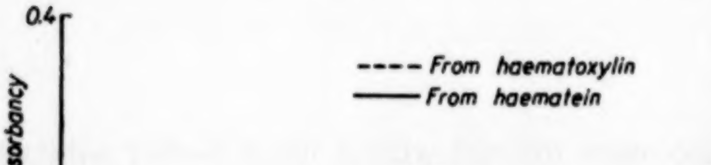

Fig. 7. Spectra of Al-complexes from haematoxylin, and from haematein

In an attempt to confirm these findings, the unsuccessful attempts made in the early part of the work, to form a complex between haematein and aluminium, were repeated, and it was found possible to prepare from haematein and aluminium a solution of complex apparently identical with that of a complex prepared from haematoxylin. Spectra of both are shown in Fig. 7. The difficulty

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experienced earlier in forming the complex with haematein is apparently due to its low solubility and the fact that it decomposes fairly rapidly under conditions which are ideal for complex formation. This deduction that haematein and not haematoxylin is the reactive agent is supported by cases of complex formation where oxidised haematoxylin is recommended as more satisfactory than the pure reagent[1,8].

Despite the conclusion that the haematoxylin reagent reacts by virtue of its conversion to haematein, haematoxylin remains the more convenient form for practical use since haematein is difficult to obtain pure and is in any case of such relatively low purity that a sufficient concentration cannot be obtained because it decomposes too rapidly in solution.

The characteristics of the complex

The aluminium complex in acid solution has a broad peak in the region of 5750 A (Fig. 6) and in alkali a much broader peak at approximately 6025 A (Fig. 4), though the shape of this peak suggests that it is possibly a combination of a peak at 5750 A and another at about 6050 A. It seems likely that both these peaks are due to the same molecular configuration which is essentially that of the haematein ion which has a peak in the region 5620 A, some modification appearing due to the presence of the aluminium.

Under alkaline conditions the complex decomposes rapidly giving some evidence of the appearance of a peak at about 4300 A which corresponds to a combination of the haematein peak and peaks arising from decomposition products.

In acid solution the complex decomposes very slowly (Fig. 6) and would give a peak corresponding to haematein except that the formation of haematein from complex is much slower than the oxidation of haematein to species H_D under these conditions. Thus in acid the decomposition proceeds directly to H_D peak 3850 A.

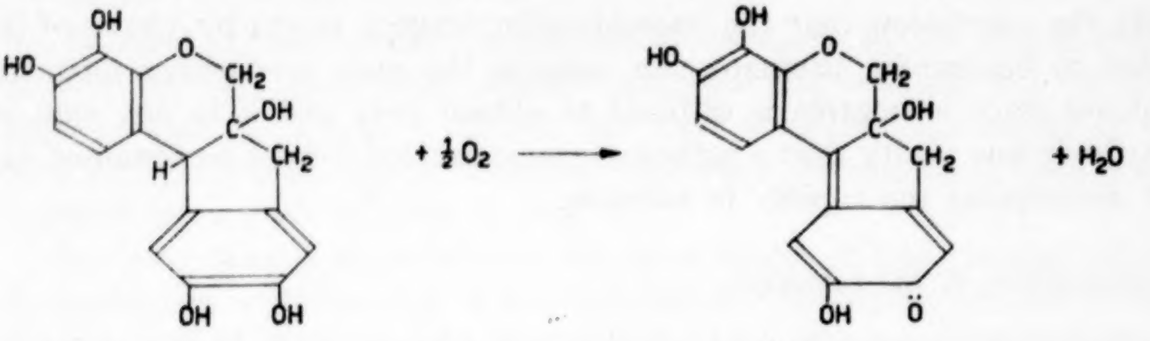
The molar ratio of aluminium to haematoxylin in the complex appears to be 1.33 (*cf.* Part I)[2] but determination of the aluminium/haematein ratio gives a figure of 2. The ratio obtained for aluminium to haematoxylin then merely indicates the amount of dye necessary to ensure the presence of sufficient haematein to complex the aluminium completely.

Mode of formation of complex

It is suggested that the apparent combination of aluminium with haematoxylin is governed by the following set of reactions.

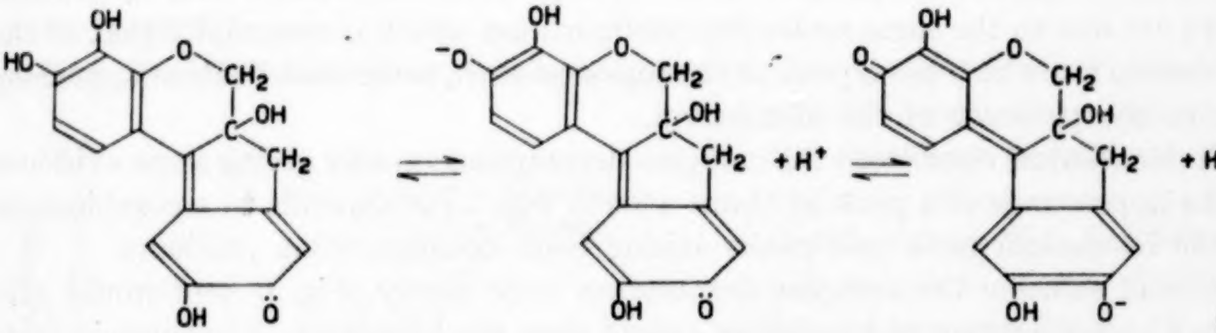
The haematoxylin is first oxidised to haematein (Equation A); in the solution, at the concentration used, there is always enough dissolved oxygen present to form sufficient haematein for the subsequent reactions with aluminium. This oxidation is relatively slow in acid solution and freshly prepared acid solutions of haematoxylin do not react with aluminium. Oxidation is more rapid in alkali, but even under these conditions freshly prepared haematoxylin shows only a fraction of the reactivity of an aged solution.

The second stage is the ionisation of the haematein and corresponds to the appearance of the 5620 A peak. (Equation B).


OH
HO
O
CH₂
OH
C
H
CH₂
OH
OH
+ ½ O₂
OH
HO
O
CH₂
OH
C
CH₂
+ H₂O
OH
Ö

(A)

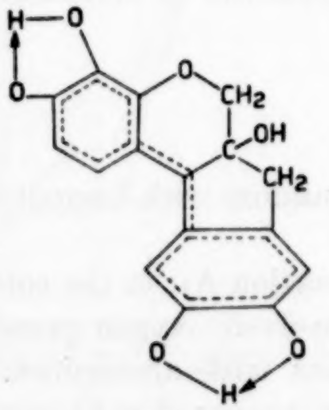
(I) (II)


OH
HO
O
CH₂
OH
C
CH₂
OH
Ö
OH
⁻O
O
CH₂
OH
C
CH₂ + H⁺
OH
Ö
OH
O
O
CH₂
OH
C
CH₂
+ H⁺
OH
O⁻

(B)

(II) (III) (IV)

The ionised haematein will possess two possible resonance forms (III, IV) and these account for the intense colour of the ionic solution. The actual structure of the haematein ion will approximate to something between the two structures (III) and (IV) and will be similar to (V).


H—O
O
O
CH₂
OH
C
CH₂
O
O
H

(V)

Formation of the dye complex may then take place by one of the following mechanisms each of which preserve and stabilise the essential electronic configuration of the haematein ion.

In the following equations only one of the reactive ends of the molecule (V) is shown, the reaction at the other end of the molecule being essentially the same.

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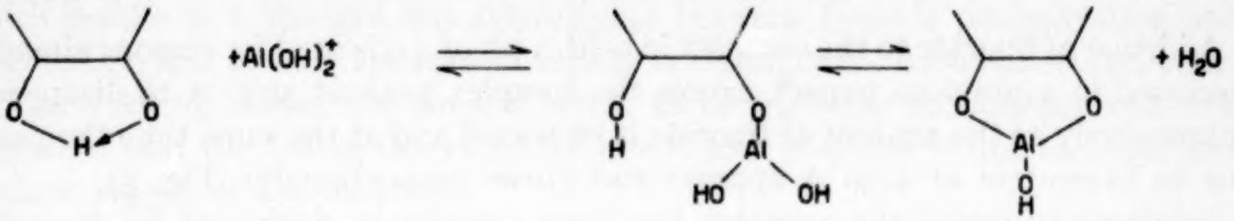
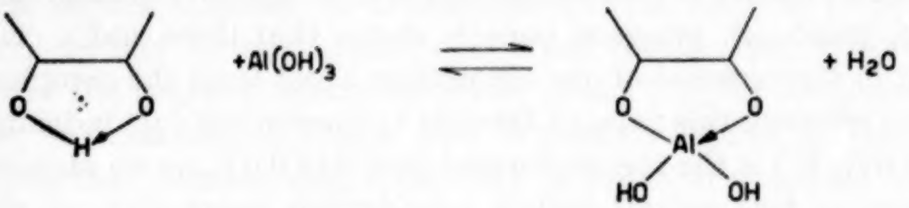
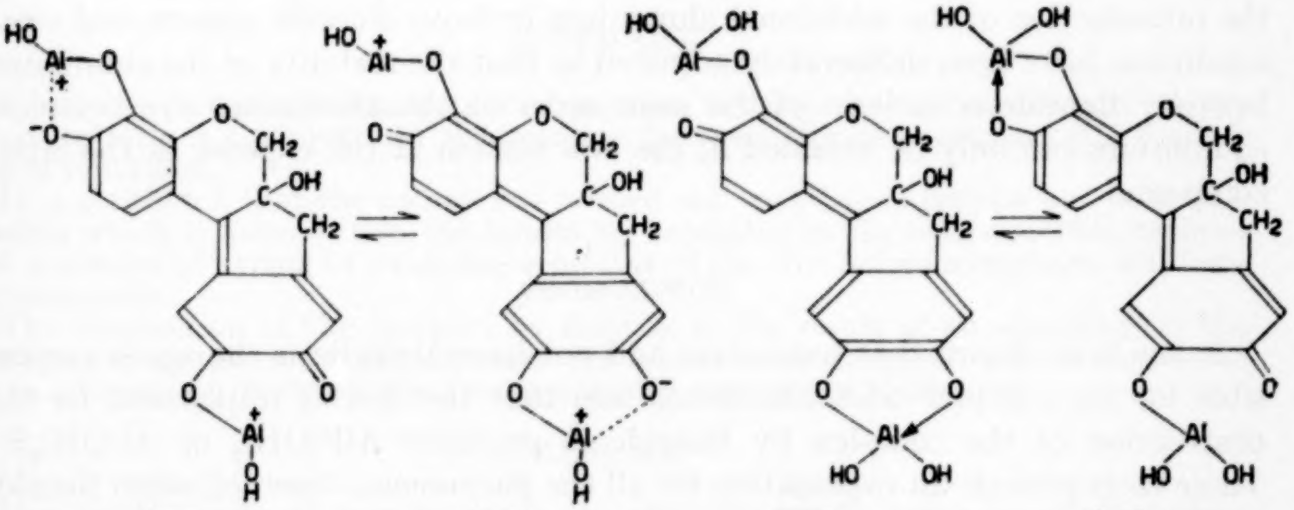
Reaction 1



Reaction 2



In the respective cases the resonance forms of the molecule will approximate to (VI) and (VII) for reaction 1 and (VIII) and (IX) for reaction 2.



(VI) (VII) (VIII) (IX)

There appears to be no method at the moment for distinguishing between these two reactions; in fact it is possible that both occur, reaction 2 predominating under alkaline conditions and reaction 1 being the main mechanism in acid.

It seems unlikely that the reaction involves unionised haematein since this would involve either different reactions at each end of the molecule or a tautomeric change involving a transitory ionisation; the latter case would approximate to the reaction with ionised haematein. Since the pKa of haematein is 6.5 even at a pH of 4.5, there would be sufficient of the ion present for the suggested reactions to take place. At a pH of about 3.5 and below no reaction takes place.

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The destruction of complex by fluoride

Addition of fluoride to the complex in acid, a pH of 4.9 is used for reasons already discussed in a previous paper[2], causes the complex peak at 5670 A to disappear progressively as the amount of fluoride is increased and at the same time the peak due to haematein at 4430 A appears and grows proportionally (Fig. 5).

Solutions in which the complex has been completely destroyed by fluoride, if kept, show a gradual loss of the haematein peak 4430 A whilst the peak at 3850 A due to an oxidation product of haematein H_D grows progressively (Fig. 5a).

A typical calibration graph (*cf.* previous paper[2]) shows that three and a half atoms of fluoride result in the removal of one aluminium atom from the complex. In the light of BROSSETT's[14] work this ratio of fluoride to aluminium ($3\frac{1}{2}$) indicates that $Al(OH)_2F$ (or $Al(OH)_3F^-$) is the species formed (not $Al(OH)F_2$ as we suggested in the previous paper of this series)[2] with a considerable proportion of the fluoride in solution, present as the uncombined ion. This assumes as is not unlikely that under the chosen conditions the stability of the hydroxy fluorides is not greatly different from that of the aluminium fluorides.

The addition of fluoride then to a solution of the aluminium dye complex results in an upsetting of the aluminium-hydroxy-dye-complex equilibrium by the introduction of the additional aluminium-hydroxy-fluoride system and since conditions have been deliberately adjusted so that the stability of the aluminium hydroxy fluoride is at least of the same order as the aluminium dye complex, equilibrium can only be attained in the new system at the expense of the latter compound.

CONCLUSIONS

It has been shown that haematein and not haematoxylin is the agent responsible for the complex with aluminium and that the species responsible for the destruction of the complex by fluoride is probably $AlF(OH)_2$ or $Al(OH)_3F^-$. These facts provide an explanation for all the phenomena observed when fluoride is determined with the aluminium haematoxylin reagent. The systems, aluminium-hydroxyl-dye and aluminium-hydroxyl-dye-fluoride, are complicated by the tendency of the haematein to undergo further oxidation. To complete this work a study of the dye complex equilibrium is needed but the instability of haematein renders the system unsuitable; other similar systems using more simple dyes have been found, however, which will enable such a study to be made. It is also intended to attempt a study of the aluminium-hydroxy-fluoride system which may help further to elucidate the problem.

As a result of this work and that previously reported, the recent paper of PRICE AND WALKER[1] contains some differences and one error. These authors measure the transmissions of the various fluoride solutions against a water blank and obtain a curve on calibration, whereas in the present work measurements are

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made in terms of absorbancy against a blank containing reagent but no fluoride which results in a straight line relationship between fluoride concentration and absorbancy, and in addition reagent effects are eliminated. Ammonium carbonate has been found, during the present work, to be perfectly satisfactory and it is suggested that the fading described by PRICE AND WALKER is due to impurities in their supply of the material.

The species formed between aluminium and fluoride under the conditions of the method cannot be AlF_6^{-3} as stated by PRICE AND WALKER. Calculation from their figures indicate an aluminium/fluoride ratio of $1:2\frac{1}{2}$-3 which leads to a result similar to that already reported herein. Also the ratio of aluminium to dye in the reagent, which should be about 1.33 for haematoxylin or 2 for haematein, is according to PRICE AND WALKER's figures of the order of seven; this means that considerable sensitivity is lost and accounts for the fact that their method is six times less sensitive than that described in the first paper[2] of this series.

ACKNOWLEDGEMENT

The authors wish to thank the Chief Scientist, British Ministry of Supply, for permission to publish this paper.

SUMMARY

A spectrophotometric study of the reaction between haematoxylin and aluminium to form a complex and the reaction between this complex and the fluoride ion is described.

It is concluded that the complex is formed not with haematoxylin but with haematein which is formed from the former by oxidation in the solution. This explains the necessity of ageing or oxidising solutions of the dye before complexes will form satisfactorily.

The destruction of the complex by fluoride is the result of an alteration in the equilibrium conditions resulting from the addition of that ion and the formation of an aluminium hydroxy fluoride containing one atom of fluorine.

RÉSUMÉ

Une étude spectrophotométrique a été effectuée sur la formation du complexe hématoxyline-aluminium et sur la réaction entre ce complexe et l'anion fluorhydrique. On arrive à la conclusion que le complexe n'est pas formé par l'hématoxyline, mais par l'hématine, produit d'oxydation de l'hématoxyline, en solution. Ceci explique la nécessité de travailler en solution oxydante.

La destruction du complexe par l'anion fluorhydrique provient d'un changement des conditions d'équilibre résultant de la formation d'un hydroxyfluorure d'aluminium, renfermant un atome de fluor.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Untersuchung der Reaktion zwischen Hämatoxylin und Aluminium, die zur Bildung eines Komplexes führt, und der Reaktion dieses Komplexes mit Fluoridionen beschrieben.

Es wurde gefolgert, dass der Komplex nicht mit Hämatoxylin, sondern mit Hämatein gebildet wird, das aus dem ersteren durch Oxydation in der Lösung ge-

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bildet wird. Dadurch wird auch die Notwendigkeit der Verwendung von älteren oder oxydierten Farbstofflösungen zur befriedigenden Bildung des Komplexes erklärt. Die Zerstörung des Komplexes mit Fluorid wird durch eine von der Addition dieses Ions und der Bildung eines 1 Fluoratom enthaltenden Aluminiumhydroxyfluorids herrührenden Veränderung der Gleichgewichtsbedingungen verursacht.

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ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM*

by

J. J. KIRKLAND** AND JOHN H. YOE

Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia,
Charlottesville, Virginia (U.S.A.)

INTRODUCTION

Complex halide anions have been widely utilized for the colorimetric determination of certain metals by measurement of their absorption maxima occurring in the visible spectral region[1-7]. Few methods have been developed, however, in which the spectrophotometric measurement is made in the ultraviolet[8,9].

A sensitive spectrophotometric procedure is proposed for the determination of small amounts of platinum. The method is based upon the measurement of a strong ultraviolet absorption maximum characteristic of the $PtCl_6^{-2}$ ion.

REAGENTS

Platinum wire obtained from the American Platinum Works and specified 99.9% pure was examined spectroscopically for impurities. Faint lines due to copper and silver were noted, indicating only traces of these metals. A standard chloroplatinate solution was prepared by dissolving 1.000 g of the pure platinum in 50 ml of aqua regia. The solution was evaporated almost to dryness and then treated with three successive 10 ml portions of 1:1 distilled water-concentrated hydrochloric acid, each time evaporating almost to dryness in order to free oxides of nitrogen. The final solution was taken up in distilled water containing about 4 ml of concentrated HCl and made up to 100 ml volume. This gave a stock solution that was about $0.5M$ in HCl and 10 mg/ml in platinum; it was standardized gravimetrically[10] and found to contain 9.99 mg of platinum per ml. Platinum solutions of lower concentration were prepared by appropriate dilutions. Standard solutions of less than 100 p.p.m. were made up fresh daily because it was found that they slowly decreased in concentration upon standing.

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* From the Ph.D. dissertation of J. J. KIRKLAND (Virginia, 1953).

** Present address: Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

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In determining the effect of pH on the intensity of the absorption band characteristic of $PtCl_6^{-2}$, the following buffers were used[11]:

Buffer	pH
HCl—KCl	2.0
HCl—KCl	3.1
CH_3COOH—CH_3COONa	4.9
NaOH—KH_2PO_4	6.3
NaOH—KH_2PO_4	7.6
NaOH—KCl—H_3BO_3	8.8

The acetic acid-sodium acetate and hydrochloric acid-sodium acetate buffers utilized in the Procedure were prepared by mixing 2*M* solutions of each constituent in the proper ratios.

Stock solutions of the metal chlorides of ruthenium, rhodium, palladium, osmium and iridium were obtained by dissolving appropriate salts of high purity. In some cases it was necessary to make these solutions acid in order that no change in concentration would occur due to hydrolysis or basic salt formation.

APPARATUS

All measurements were made with a Beckman spectrophotometer, Model DU, using matched 1 cm quartz cells. The instrument was operated at constant sensitivity and slit widths of 0.3-0.7 mm, corresponding to effective band widths of about 0.3-2 mμ.

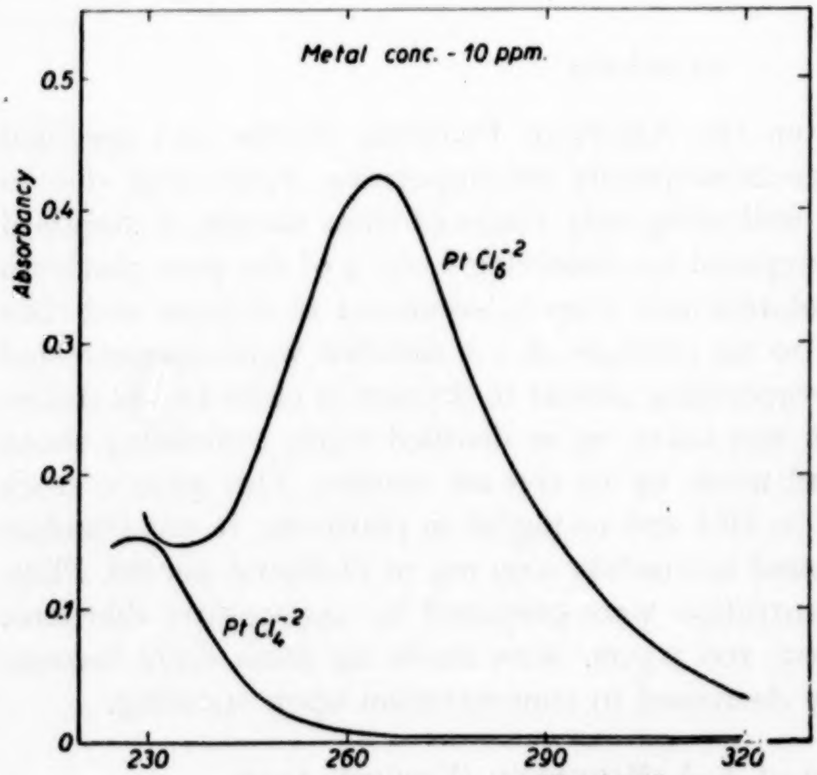

Fig. 1. Absorption curves of platinum ions.

EXPERIMENTAL

The ultraviolet spectrum of $PtCl_6^{-2}$ ions exhibits an intense absorption at 262 mμ even at very low platinum concentrations; $PtCl_4^{-2}$ ions in similar amounts show negligible absorbancy at this wavelength (Fig. 1). In order to evaluate the possibility of utilizing the $PtCl_6^{-2}$ absorption maximum as a means of determining small amounts of the metal, a study of some

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of the important characteristics of the absorption band was undertaken.

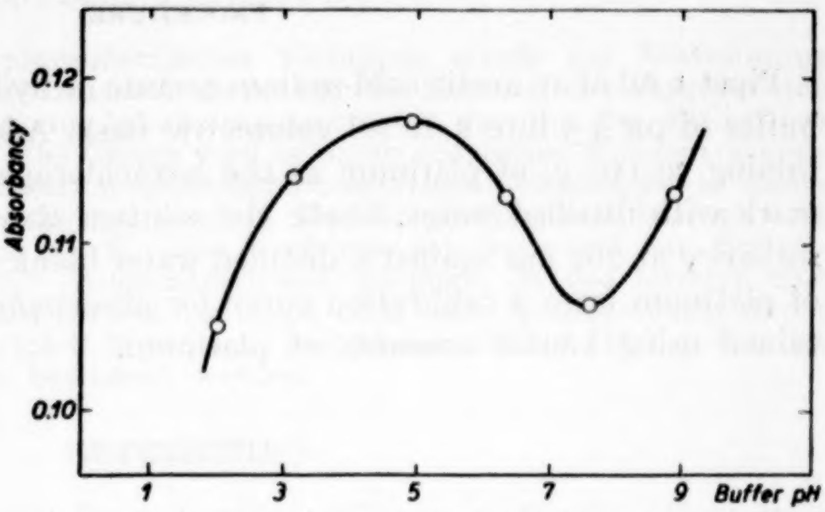

Fig. 2. Effect of pH on the intensity of the $PtCl_6^{-2}$ absorption maximum.

Effect of pH. There is very little change in the intensity of the 262 $m\mu$ maximum in the pH range 3.5 to 6, as illustrated in Fig. 2. It was found convenient in the analytical procedure to buffer the sample solutions at about pH 5 with either sodium acetate-acetic acid or sodium acetate-hydrochloric acid buffers. Phthalate buffers are unsuited because of the strong ultraviolet absorption which the phthalate structure displays.

Beer's Law and sensitivity. Adherence to Beer's law was observed in the concentration range investigated. The sensitivity of the proposed method is 0.05 p.p.m. in a 1-cm cell, or 0.017 γ Pt/cm² by the Sandell notation[1]. The concentration for most accurate spectrophotometric measurement is 3-11 p.p.m.

Precision of measurement and stability of absorption maximum. Absorbancy measurements of buffered $PtCl_6^{-2}$ solutions at 262 $m\mu$ can be made with a precision of ± 1%. These mixtures were found to be stable for several hours before a slow decrease in the intensity of the absorption maximum is apparent.

Effect of diverse ions. Absorption spectra of the chloride anions of the platinum metals were taken in the region 220-400 $m\mu$. These anions had absorptions of varying intensities at 262 $m\mu$. Concentrations of the various platinum metal chlorides that can be present without causing a relative increase of more than 3% in the measurement of a 10 p.p.m. platinum solution are as follows:

Rh — 0.05 p.p.m.
Ru — 0.08 p.p.m.
Pd — 0.1 p.p.m.
Ir — 0.3 p.p.m.
Os — 5 p.p.m.

A number of ultraviolet absorption spectra of other transition metal salts were recorded; most of these showed absorption at 262 $m\mu$ which would inferere with a quantitative measurement of the $PtCl_6^{-2}$ band.

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PROCEDURE

Pipet 1 ml of an acetic acid-sodium acetate or hydrochloric acid-sodium acetate buffer of pH 4-5 into a 10 ml volumetric flask. Add the sample, preferably containing 30-110 γ, of platinum as the hexachloroplatinate ion and dilute to the mark with distilled water. Shake the solution thoroughly and measure its absorbancy at 262 mμ against a distilled water blank. Determine the concentration of platinum from a calibration curve (or absorbancy index) which has been obtained using known amounts of platinum.

APPLICATION

It is apparent that successful analytical application of the ultraviolet band due to the $PtCl_6^{-2}$ ion would necessitate a fairly complete separation of platinum from interfering substances; however, even though considerable interference by most metals commonly occurring with platinum is noted, the method should be useful because of its convenience, simplicity, high sensitivity and good precision. The authors have found the procedure particularly suited for the determination of the concentrations of $PtCl_6^{-2}$ and $PtCl_4^{-2}$ ions in solution. Since $PtCl_4^{-2}$ has negligible absorbancy at 262 mμ, its concentration can be determined by subtracting the amount of $PtCl_6^{-2}$ found by the ultraviolet measurement from the total platinum concentration.

SUMMARY

A sensitive spectrophotometric procedure has been developed for the determination of small amounts of platinum. It is based upon the measurement of the strong ultraviolet absorption maximum at 262 mμ which is characteristic of the $PtCl_6^{-2}$ ion. Beer's law is obeyed over a useful range in concentration, 3-11 p.p.m. being the range of most accurate spectrophotometric measurement. The sensitivity is 0.05 p.p.m. and the precision $\pm$ 1%. The procedure is particularly suited for the determination of the concentrations of $PtCl_6^{-2}$ and $PtCl_4^{-2}$; since the latter has negligible absorbancy at 262 mμ, its concentration can be determined by subtracting the amount of $PtCl_6^{-2}$ found by the ultraviolet measurement from the total platinum concentration.

RÉSUMÉ

Une méthode spectrophotométrique sensible a été établie en vue du dosage de petites quantités de platine. Elle est basée sur la mesure dans l'ultraviolet de l'absorption maximum à 262 mμ, caractéristique pour $PtCl_6^{-2}$. La courbe obtenue obéit à la loi de Beer sur une longueur suffisante, 3 à 11 p.p.m. étant les concentrations favorables pour des mesures spectrophotométriques les plus précises. La sensibilité est de 0.05 p.p.m. et la précision $\pm$ 1%. Ce procédé convient particulièrement bien pour la détermination des concentrations de $PtCl_6^{-2}$ et $PtCl_4^{-2}$; ce dernier présentant une absorption négligeable à 262 mμ, sa concentration peut être déterminée par différence entre la teneur en $PtCl_6^{-2}$ trouvée (par mesure dans l'ultraviolet) et la concentration totale en platine.

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ZUSAMMENFASSUNG

Ein empfindliches spektrophotometrisches Verfahren wurde zur Bestimmung von geringen Mengen Platin entwickelt. Es ist auf die Messung des ausgeprägten Ultraviolett-Absorptionsmaximums bei 262 mμ gegründet, das für das $PtCl_6^{-2}$-Ion charakteristisch ist. Das Beer'sche Gesetz wird in einem nützlichen Konzentrationsbereich befolgt, wobei die genauesten spektrophotometrischen Messungen in einem Bereich von 3-11 Millionstel erhalten werden. Die Empfindlichkeit beträgt 0.05 Millionstel und die Genauigkeit ± 1%. Das Verfahren ist besonders zur Bestimmung der $PtCl_6^{-2}$ und $PtCl_4^{-2}$ Konzentrationen geeignet; da das letztere eine zu vernachlässigende Absorption bei 262 mμ zeigt, kann seine Konzentration durch Subtraktion der durch Ultraviolett-Messungen gefundenen $PtCl_6^{-2}$ -Menge von der gesamten Platinkonzentration bestimmt werden.

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IRON, CHROMIUM AND ALUMINIUM PHTHALATE COMPLEXES AND THEIR APPLICATION TO THE DETERMINATION OF THE METALS

A HETEROMETRIC STUDY

by

M. BOBTELSKY AND I. BAR-GADDA

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem (Israel)

INTRODUCTION

The heterometric method[1] was developed during the past four years by the first author with co-workers. The instrument ("Heterometer") was continuously improved and adapted to the new problems which arose in the quantitative study of different heterogenous reactions. The results of each heterometric study are represented by "heterometric titration curves". During this period about 13,000 such curves were taken and their character studied.

Each heterometric curve contains at least three *critical endpoints:* the point of *initial* precipitation, the optical density *maximum* point and the point of complete *dissolution*. Most of the curves have some additional critical points which may be used for the study of the *partial* reactions which proceed during a heterometric titration. The curves obtained give a presentation on a quantitative basis of the reactions proceeding simultaneously in the *solution* and in the *solid* state. The endpoints are valid for both phases. Heterometry deals with *endpoints* and is *not* concerned with the particle size. Particles of either *unit* or *different* size may be present.

The heterometric method was developed chiefly for the study of heterogenous chemical reactions. Later on, the experience and knowledge gained, provided a basis for special studies of *analytical* reactions. In this branch our intention was to develop methods to replace micro- and ultramicro-gravimetric analysis.

The following study constituted part of a research carried out on complexes of carboxylic acids with different cations. Many studies exist on complexes of oxalate with trivalent cations, but little research is available on other dicarboxylic complexes. Some indications of the existence of phthalate complexes of iron and chromium are given by the study of mutarotation[2]. Complexes of chromium with oxalate, phthalate, succinate, malonate and maleate[3], which are of importance to the leather industry, were established by conductometric measurements.

EXPERIMENTAL

The instrument used in this study was the "Heterometer" built by the first author. The description of the instrument and of heterometric titrations are given elsewhere[1]. The salts used were all C. P. Baker's. Molar stock solutions of the salts were prepared. The temperature varied between 20° and 27° C.

RESULTS

Iron. Fig. 1 shows the composition and results of a selection of heterometric titrations which were carried out in 50% alcoholic solution (or 90%) by the addition of alcoholic $FeCl_3$ solution to an alcoholic solution of potassium phthalate (iron phthalate is soluble in water). In all the titrations which were carried out in vessels of two different diameters, a clear solution is obtained at first. Only when the ratio of 3[phthalate] : 1[Iron] (=$[Fe(III)Phth_3]^{-3}$) is reached, a precipitation begins. The density then rises, and the optical maximum density is reached exactly at the ratio of 1[Phth] : 1[Fe(III)] (curves 1 and 2.). No further change in density occurs. Curve 1 is clearly composed of two parts, indicating that an insoluble intermediate (=$Fe(III)_2Phth_3$) exists which is then transformed by an excess of iron into the insoluble compound $[Fe(III)Phth]_n$. Fig. 2 shows results

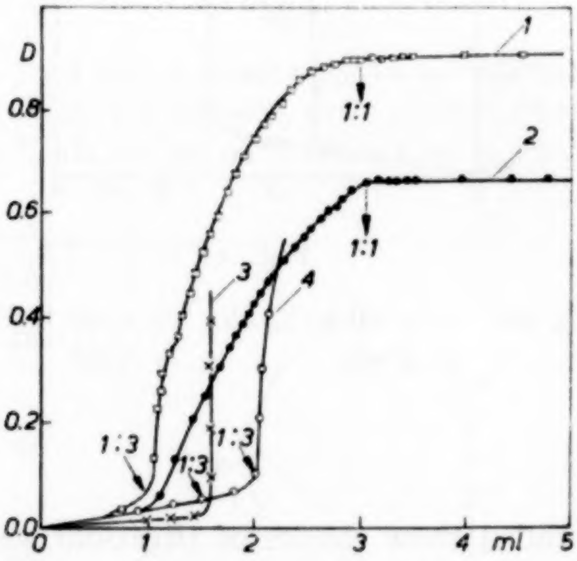

Fig. 1

1. 3 ml K_2Phth 0.05M 50% alc. + 7 ml 50% alc. +x ml $FeCl_3$ 0.05M 50% alc.
2. 3 ml ,, ,, ,, ,, +17 ml ,, ,, +x ml ,, ,, ,,
3. 2 ml ,, 0.1M + 8 ml H_2O +x ml ,, ,, dans H_2O
4. 3 ml ,, ,, 50% alc. + 7 ml 50% alc. +x ml ,, ,, 50% alc.

of reverse titrations. Here the titrations (in contrast to those presented in Fig. 1, curves 1 and 2, which proceed very slowly) proceed very fast and are completed in about 15 minutes. At first a solution (1 Phth : 1 Fe(III)?) is obtained. The maximum density is reached exactly at the molar ratio of 3[Phth]:2[Fe(III)](= $Fe(III)_2Phth_3$) and no further change occurs. The latter may be presented as Fe(III) $[Fe(III)Phth_3]$↓. Nothing definite can be said about the structure of the insoluble $[Fe(III)Phth]_n$↓ (Fig. 1) which is probably an iron salt of the iron phthalate anion.

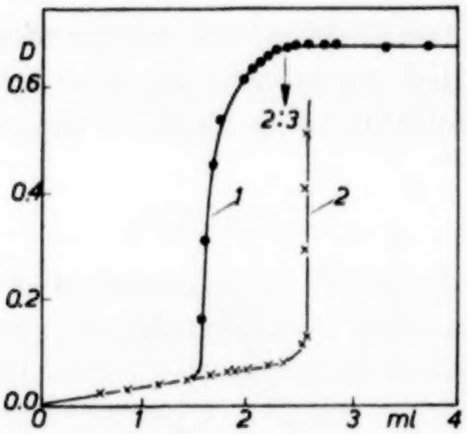

Fig. 2

1. 3 ml $FeCl_3$ 0.05*M* 50% alc. + 7 ml 50% alc. + x ml K_2Phth 0.1*M* 50% alc.
2. 6 ml ,, ,, ,, + 4 ml ,, + x ml ,, ,, ,,

Aluminium. Figs. 3 and 4 show results of titrations similar to those of iron carried out in 50% or 90% alcoholic solutions. On addition of phthalate to aluminium (Fig. 3) a solution of the soluble complex $[AlPhth_2]^-$ is obtained quantitatively at first. Exactly at the molar ratio of 2[Phth] : 1[Al] the density curve rises abruptly. Maximum density is obtained at the approximate ratio of 3[Phth] : 1[Al]. The insoluble $K_3[AlPhth_3]$ is probably formed and is precipitated quantitatively. In the reverse titrations, the addition of aluminium to the phthalate solution (Fig. 4), the density rises linearily from the beginning until the maximum is reached. The latter is obtained at the molar ratio of 2[Phth] : 1[Al]. (It is remarkable that at this ratio, in Fig. 3, the precipitation just begins.) On further addition of aluminium the precipitate dissolves completely at the ratio of 3[Phth] : 2 [Al] (= $[Al_2Phth_3]^\circ$). As to the structures of the compounds obtained, the following may be said: the coordination number of aluminium towards phthalate is either four or six, but there may still exist a cation-complex $[AlPhth]^+$ which cannot be detected heterometrically. The soluble $[Al_2Pht_3]^\circ$ may be presented as an undissociated covalent molecule.

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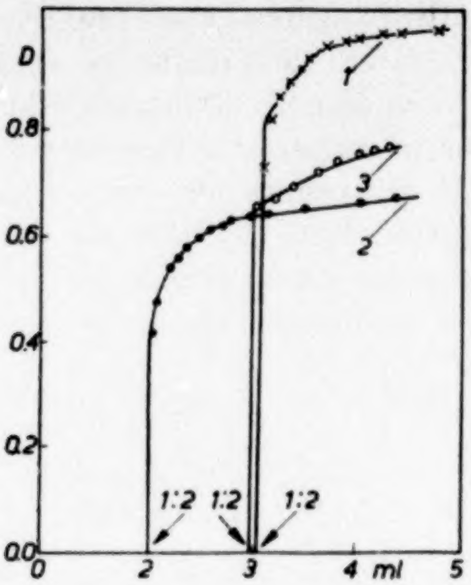

Fig. 3

1. 3 ml Al Cl_3 0.05M + 5 ml alc. + 2 ml H_2O +x ml K_2Phth 0.1M 50% alc.
2. 1 ml ,, 0.1M 90% alc. +9 ml 90% alc. +x ml K_2Phth 0.1M 90% alc.
3. 3 ml ,, 0.05M 90% alc. +7 ml 90% alc. +x ml K_2Phth 0.1M 90% alc.

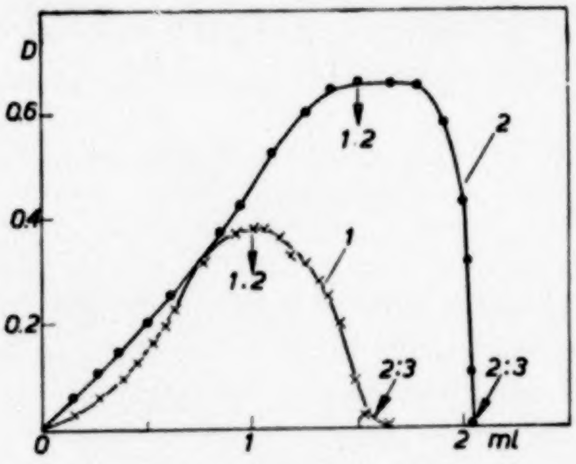

Fig. 4

1. 2 ml K_2Phth 0.1M 90% alc. +8 ml 90% alc. +x ml $AlCl_3$ 0.1M 90% alc.
2. 3 ml ,, ,, ,, ,, +7 ml ,, ,, +xml ,, ,, ,, ,,

Chromium. Fig. 5 shows the results of two such titrations taken from a series. The titrations were made with a green filter. The curves are complicated as the clear solutions by themselves gave a slight absorption (see first part of curve 1 and last part of curve 2). The titration proceeds very quickly (the solution was a 90% alcoholic one). On addition of phthalate to chromium (curve 1) a clear solution is obtained at first. Exactly at the ratio 2[Phth] : 1[Cr(III)]

(= [Cr(III)Phth$_2$]$^-$) the density begins to rise abruptly until the maximum which is obtained at the ratio 3[Phth] : 1[Cr(III)] (= [Cr(III)Phth$_3$]$^{-3}$ or K$_3$[Cr(III)-Phth$_3$]$\downarrow$). The behaviour is similar to aluminium, but in the case of chromium, the excess phthalate seems to dissolve the precipitate again. Table I summarises these results. Curve 2 shows the results obtained by the gradual addition of chromium to the phthalate solution. Here too, as in the case of aluminium, the density increases linearily until the maximum which lies at 3[Phth] : 1[Al]. An excess of chromium dissolves the precipitate again.

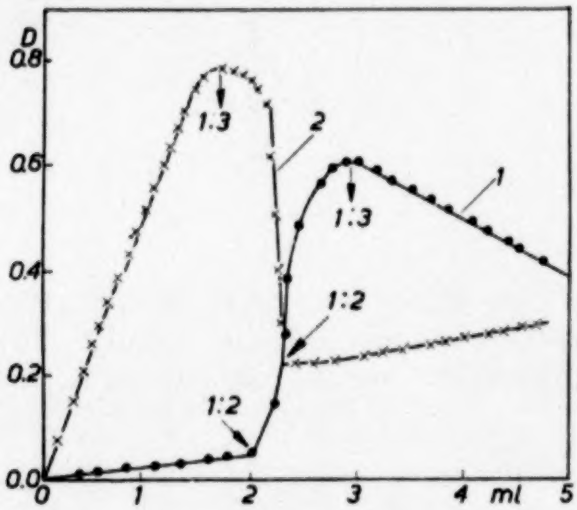

Fig. 5

1. 4 ml Cr (NO$_3$)$_3$ 0.025M 90% alc. +6 ml 90% alc. +x ml K$_2$Phth 0.1M 90% alc.
2. 2 ml K$_2$Phth 0.1M ,, ,, +8 ml ,, ,, +x ml Cr (NO$_3$)$_3$ 0.05M 90% alc.

Mixtures. In order to get a further insight into the compounds obtained and their behaviour under different working conditions, we present a small selection of further experiments with mixtures of two or three cations. The following absorption curves are most interesting as each of them gives detailed information of the partial reactions which occur while the heterometric titration is carried out. Fig. 6 shows the results of such titrations, which were carried out by the dropwise addition of phthalate to the mixture of two (curves 1 and 2) or three (curve 3) metals. In all cases one of the metals was iron. All the curves obtained are of similar character. Each curve is composed of two vertical and two horizontal branches. The greater part of each curve is of an S shape. Four breaks appear in each curve. Each break indicates the *end* of one reaction and the similar *beginning* of another. The breaks are marked on the curves by arrows. On addition of phthalate, a saturated solution is obtained at first. At a certain point the iron begins to precipitate and the density rises until the first maximum point is obtained (curve 1 and 2) exactly at the molar ratio of 2[Phth] : 1[Fe(III)]. Just at this point a new reaction between the aluminium and an excess of phthalate begins

in solution. At the second break $[Al_2Phth_3]^\circ\uparrow$ is formed quantitatively in solution. (In curve 3 both $[Al_2Phth_3]^\circ$ and $[Cr_2Phth_3]^\circ$ are formed simultaneously in solution). During the following S curve (between the second and fourth breaks) the following two reactions occur:

$$(1)\quad K[Fe(III)Phth_2]\downarrow + K_2Phth \longrightarrow K_3[Fe(III)Phth_3]\downarrow$$
$$(2)\quad [Al_2Phth_3]^\circ\uparrow + K_2Phth \longrightarrow 2\ K[AlPhth_2]\downarrow$$

In case 3 a similar reaction to (2) occurs with the chromium. That part of the titration represented by the S-graph takes most of the time (60—90 min) needed for the whole titration (probably because reaction (1) proceeds in a heterogenous system). As both reactions (1 and 2) give two *different* density curves, we obtain an S-curve with an inflexion point. The last maximum point is obtained when all the reactions are completed. The maximum point (fourth break) conforms therefore to the sum of the above reactions (1+2). As many experiments showed, the above curves are obtained only under the following conditions: 1) the molar concentration of iron (or chromium) must be less or at most equal to the concentration of the other metal and 2) the aluminium concentration is within 1-3

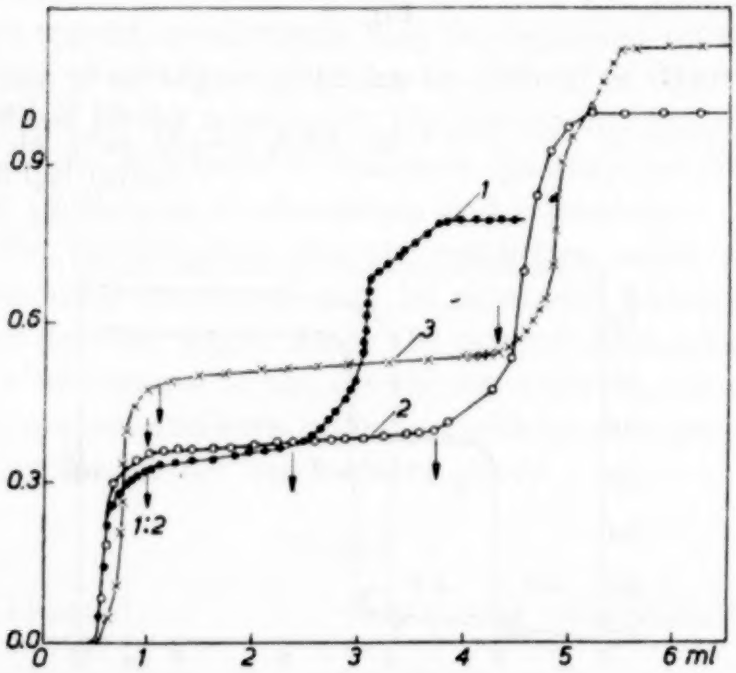

Fig. 6

1. 1 ml $FeCl_3$ 0.05*M* 50% alc. + 2 ml $AlCl_3$ 0.05*M* 50% alc. + 7 ml 50% alc. + x ml K_2Phth 0.1 *M* 50% alc.
2. 1 ml $FeCl_3$ 0.05*M* 50% alc. + 4 ml $AlCl_3$ 0.05*M* 50% alc. + 5 ml 50% alc. + x ml K_2Phth 0.1*M* 50% alc.
3. 1 ml $FeCl_3$ 0.05*M* 50% alc. + 2 ml $Cr(NO_3)_3$ 0.05*M* 50% alc. + 2 ml $AlCl_3$ 0.05*M* 50% alc. + 5 ml 50% alc. + x ml K_2Phth 0.1*M* 50% alc.

times more than the iron. Solutions which contain higher iron concentrations give only the iron curve (=$Fe(III)_2Phth_3$, compare Fig. 7, curves 1 and 2), while the aluminium part is almost unnoticeable. We shall not present the results obtained in the presence of iron+chromium, since they are subject to the same restrictions as iron+aluminium. Fig. 8 brings results of similar titrations of a mix-

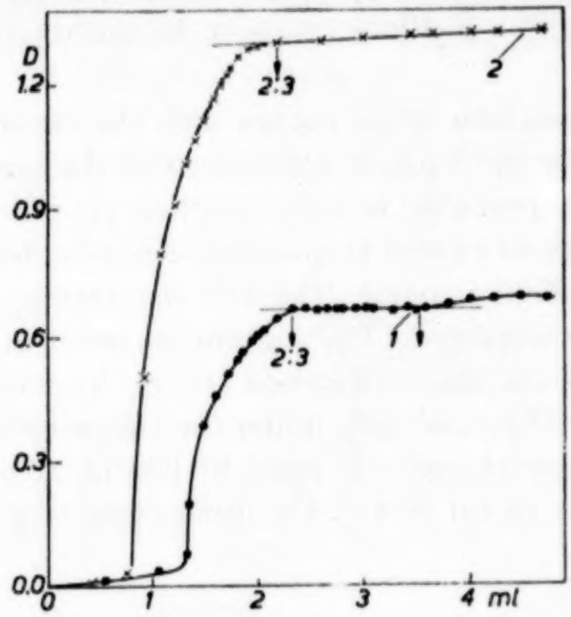

Fig. 7

1. 6 ml $FeCl_3$ 0.05*M* 50% alc. +2 ml $AlCl_3$ 0.05*M* 50% alc.+12 ml 50% alc. +x ml K_2Phth 0.2*M* 50% alc.
2. 6 ml ,, ,, ,, ,, +2 ml $AlCl_3$ 0.05*M* 50% alc.+2 ml 50% alc. +x ml K_2Phth 0.2*M* 50% alc.

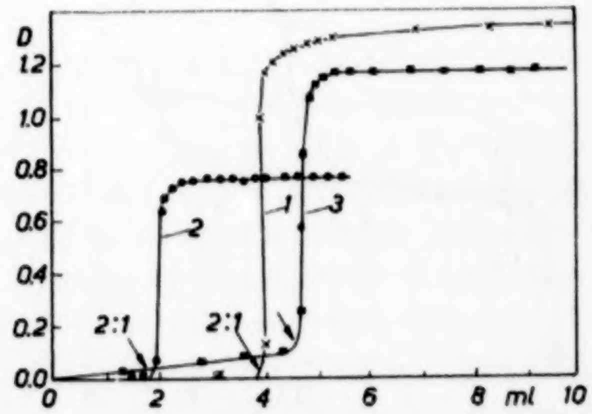

Fig. 8

1. 6 ml $AlCl_3$ 0.05*M* 50% alc.+2 ml $Cr(NO_3)_3$ 0.05*M* 50% alc.+2 ml 50% alc. +x ml K_2Phth 0.2*M* 50% alc.
2. 2 ml ,, ,, ,, ,, +2 ml $Cr(NO_3)_3$ 0.05*M* 50%alc.+6 ml 50% alc. +x ml K_2Phth 0.2*M* 50% alc.
3. 2 ml ,, 0.1*M* ,, ,, +2 ml $Cr(NO_3)_3$ 0.1*M* 50% alc.+6 ml 50% alc. +x ml K_2Phth 0.2*M* 50% alc.

ture of aluminium and chromium in absence of iron (a blue filter was used). In all cases a clear solution is obtained at first. *Exactly* at the point when the molar ratio of phthalate to the sum or $[\mathrm{Al}]+[\mathrm{Cr}]$ is equal to 2 : 1 the density rises abruptly very high and a white precipitate is formed. This occurs only then, when the aluminium concentration is equal or higher than that of chromium. The last titrations proceed very fast and constant readings of the galvanometer are obtained instantly.

DISCUSSION AND CONCLUSIONS

The above experimental material shows that under suitable working conditions (which may be derived from the curves) we may obtain quantitatively in the case of iron one of the following three complexes: $[\mathrm{Fe(III)Phth}]^+$, $[\mathrm{Fe(III)Phth_2}]^-$ or $[\mathrm{Fe(III)Phth_3}]^{-3}$. They may be obtained either in solution or as insoluble compounds. In addition another insoluble iron compound of the empirical composition $[\mathrm{Fe(III)Phth}]_n\downarrow$ may be obtained separately. Aluminium and chromium give almost identical compounds which show similar behaviour and solubility. Under no conditions could a compound of the composition 1[Me(III)] : 1[Phth] be precipitated with aluminium or chromium. Probably the cations obtained, $[\mathrm{Me(III)Phth}]^+$, are soluble under all experimental conditions. The different solubility and different behaviour of the iron and the chromium compounds (although both are transition elements) may be explained by the following fact. The electronic state of trivalent chromium is almost as rigid as in the case of aluminium in contrast to the ferric iron. The individual character of iron is also expressed in the ability, if present in sufficient quantity, to remove the state of supersaturation of phthalates of aluminium and chromium.

The results of this investigation give the conditions under which each of the complexes or compounds concerned may be separated quantitatively and subjected to a further detailed study. As to the results obtained in mixtures, they are more complicated because of the interaction between the compounds. Phenomena of supersaturation and even colloidal problems play their role. The results are very stimulating for further heterometric study.

TABLE I

Me(III)	Titrated with	Molar ratio of phthalate to metal 3 : 1	2 : 1	3 : 2	1 : 1
Fe	iron phth	↑	↓	↓	↓ ↑
Cr	phth	↓	↑	↑	
Al	phth alum.		↕		

↓ = insoluble; ↑ = soluble

SUMMARY

Using a new "heterometric" method, a series of soluble and insoluble phthalates were obtained and their behaviour, composition and analytical application studied.

RÉSUMÉ

Une série de phtalates solubles et insolubles ont été obtenus à l'aide d'une méthode nouvelle dite „hétérométrique". Le comportement, la composition et les applications analytiques de ces phtalates ont été étudiés.

ZUSAMMENFASSUNG

Mit Hilfe einer neuen „heterometrischen" Methode wurde eine Reihe von löslichen und unlöslichen Phtalaten erhalten. Verhalten, Zusammensetzung und analytische Auswertung dieser Verbindungen wurden studiert.

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UTILISATION D'UNE ALIMENTATION À INTENSITÉ CONSTANTE POUR L'ÉTALONNAGE D'UNE SOLUTION TITRÉE D'ACIDE CHLORHYDRIQUE

par

MME J. BADOZ-LAMBLING

Laboratoire de Chimie Analytique, Ecole Supérieure de Physique et Chimie Industrielles, Paris (France)

Un des avantages de la coulométrie est la possibilité de préparer des solutions étalons sans peser de substance de référence. TUTUNDŽIĆ[1] a récemment insisté sur cette particularité. Il faut par contre s'assurer que le réactif préparé électrochimiquement est bien obtenu avec un rendement de 100% en courant. Différents auteurs ont exposé les conditions nécessaires pour obtenir ce rendement[2]. Dans le cas particulier du dosage des ions H^+, la production quantitative des ions OH^- est très aisée. Alors que l'on est généralement limité par l'intensité du palier de diffusion des substances électrolysables, il n'en est rien ici puisque le solvant lui-même contribue à la production des ces ions OH^- suivant la réaction:

$$2H_2O + 2e \rightarrow H_2 \nearrow + 2OH^-$$

Ce dosage doit donc se présenter sous un jour assez simple et permettre d'obtenir des résultats aussi précis que la volumétric classique. Le dosage coulométrique d'une solution acide a été réalisé en 1938 par SZEBELLEDY ET SOMOGOYI[3]. Ces auteurs utilisèrent un voltamètre à nitrate d'argent pour mesurer la quantité d'électricité consommée par la réaction. Plus récemment certains auteurs[4,5] dosèrent par coulométrie à intensité constante de petites quantités d'acide à 2% près environ. Enfin DEFORD, PITTS ET JOHNS[6] ont produit électrochimiquement par cette même méthode les ions OH^- en dehors de la solution à titrer: à l'aide d'un tube en T qui séparait les réactifs cathodiques et anodiques, ils envoyaient cette solution alcaline dans le récipient où était effectué le dosage. Ces auteurs obtiennent des titres exacts à 0.4 ou 0.6% près. Nous proposons ici un dosage coulométrique à intensité constante effectué directement dans la solution à titrer et fournissant un titre exact à 0.2% près.

DESCRIPTION DE L'APPAREILLAGE

Alimentation à intensité constante

Nous utilisons une alimentation à intensité constante SEFRAM. L'appareil fournit douze intensités (comprises entre 0.1 et 100 mA) dont la valeur absolue

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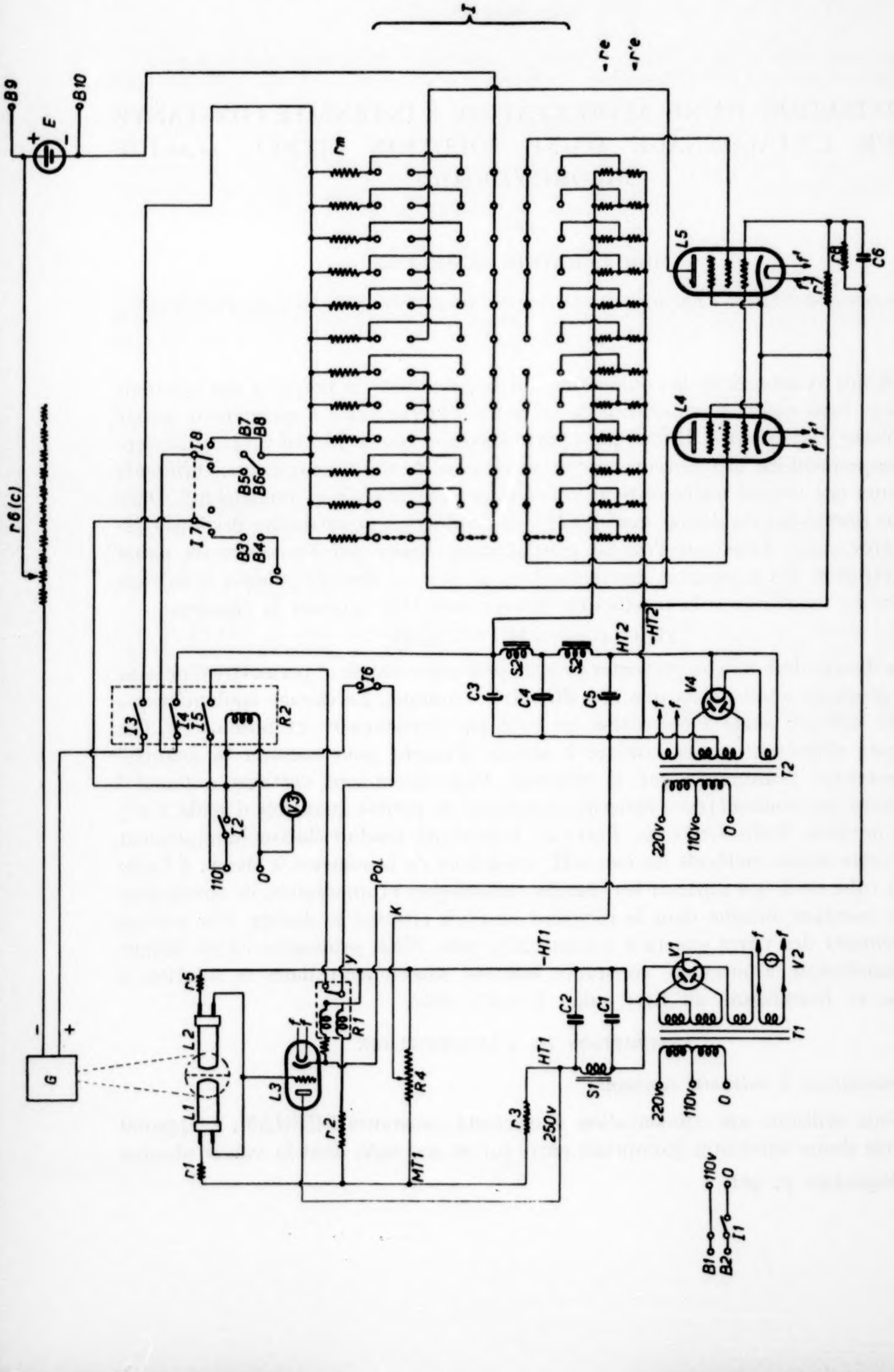
B9
B10
E
+
-
I
-r'e
-r'e
rm
r6(c)
I7
I8
B3
B4
0
B5
B6
B7
B8
L5
L4
r'
r''
r8
C6
I3
I4
I5
R2
I6
S2
S2
C3
C4
C5
HT2
-HT2
V4
f
f
T2
220v
110v
0
110
0
I2
V3
Pol
K
V
-HT1
G
-
+
L1
L2
L3
r1
r2
r3
r5
R1
R4
MT1
250v
HT1
S1
C2
C1
V1
V2
T1
220v
110v
0
B1
B2
I1
110v
0

Fig. 1. Alimentation à intensité constante.

est exacte à 0.1% près. A tout instant la chute ohmique produite par l'une de ces intensités dans une résistance étalon est opposée à la différence de potentiel d'un élément Weston: tout déséquilibre dans ce circuit d'opposition provoque la déviation du spot d'un galvanomètre qui assure l'auto-régulation. Nous avons contrôlé l'exactitude des valeurs des intensités de courant fournies par le constructeur en mesurant la différence de potentiel aux bornes d'une résistance étalon introduite dans le circuit d'électrolyse: cette détermination a été faite avec un potentiopHmètre Méci. Ce contrôle est effectué une fois pour toute.

Etant ainsi assuré de la valeur absolue de l'intensité de courant, le problème de la mesure de la quantité d'électricité revient à une simple mesure du temps. Nous utilisons un chronomètre contrôlé sur l'horloge de l'observatoire.

Nous fournissons le schéma (Fig. 1) et le principe de fonctionnement de l'appareil d'après les indications du constructeur.

L'appareil se compose de 3 parties principales et de quelques accessoires.

Pilote

L'organe pilote est un régulateur fournissant la polarisation à la deuxième partie (alimentation et rhéostat).

A partir du secteur 110 Volts, 50 périodes, branché aux bornes B1 et B2 et par l'intermédiaire de l'interrupteur général I1, un transformateur T1 fournit l'éclairage de la lampe V2 du galvanomètre G ainsi que le chauffage ff du filament de la lampe L3.

Ce transformateur également par l'intermédiaire d'une valve V1 et d'un système, de filtrage C1 S1 C2 la haute tension H.T.1. nécessaire à la lampe L3.

Une résistance chutrice r3 fournit la tension M.T.1. aux bornes de 2 cellules photoélectriques L1 — L2. Lorsque le spot du galvanomètre se déplace en éclairant plus ou moins les cellules L1 et L2, la polarisation de L3 varie; son courant de cathode varie également. Il en résulte une variation de potentiel du point Pol.

Un potentiomètre R4 permet de prélever un potentiel variable au point K.

Alimentation et rhéostat

La différence de potentiel entre les points pol. et K sert à faire varier les courants plaques des lampes L4 et L5 en fonction de la position du spot du galvanomètre.

L'alimentation de la deuxième partie de l'appareil est fournie à partir d'un transformateur T2 qui assure le chauffage f' f' des lampes L4 et L5 et qui assure l'alimentation haute tension H.T.2 fournissant le courant à la cellule d'utilisation. Cette alimentation est filtrée par les selfs S2—S2 et les condensateurs C3—C4—C5.

La Haute tension H.T.2 passant à travers le contact I4 lorsque celui-ci est fermé, traverse l'inverseur I8 (starter), soit vers la borne B8 directement, soit vers la borne B8 en passant par B5 — B6 — B7.

La cellule d'utilisation sera insérée entre les bornes B5, B6, tandis qu'un appareil de contrôle d'intensité pourra être inséré entre les bornes B7 — B8. On peut aussi court-circuiter ces deux dernières.

Le courant passe ensuite par l'une des résistances rm à destination de la plaque de la lampe L4 ou de la lampe L5, le circuit se refermant à travers la lampe pour retourner par sa cathode au moins H.T.2.

Un commutateur à 12 positions I permet de choisir la résistance rm à travers laquelle passe le courant. Les 6 premières positions du contacteur I correspondant aux faibles intensités font passer le courant à travers la lampe L4, alors que les 6 positions suivantes alimentent la lampe L5.

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La troisième galette du contacteur I permet d'alimenter les écrans soit de la lampe L4, soit de la lampe L5, à une tension convenant à chaque position, grâce aux divideurs de tension formés par les résistances re-r'e.

L'organe régulateur

L'organe régulateur est constitué par une chaîne comprenant en opposition la tension aux bornes de la résistance rm et la tension aux bornes d'une pile étalon E. Le circuit est établi par la deuxième galette du contacteur I et il se ferme à travers le cadre du galvanomètre G et le rhéostat à plots R6. (C), lorsque le contant I3 est fermé.

Si le courant traversant la résistance rm produit dans celle-ci une chute de tension exactement égale à la force électro-motrice de la pile étalon, le galvanomètre reste à son zéro.

Si le courant est plus intense, la chute de tension dans rm est supérieure à la tension de la pile étalon, le galvanomètre dévie de telle sorte que son spot illumine la cellule L2 plus que la cellule L1. Le potentiel du point pol. diminue, ce qui a pour effet de ramener le courant dans le circuit à une valeur plus basse.

Si le courant dans le circuit est plus faible que la valeur prévue, la régulation en sens inverse se produit. De la sorte, le galvanomètre travaille en méthode de zéro et lorsque R6 est amené à une résistance suffisamment faible, la régulation est excellente.

On a pu noter que des variations de tension du secteur de 20% ou des variations de résistance du simple au double de la cellule d'utilisation ne produisaient que des variations d'intensité dans la cellule nettement inférieures à 1/1,000.

D'autre part, la connaissance de la valeur exacte des résistances rm et de la force électro-motrice de la pile étalon (1.018 mV) permet de connaître la valeur absolue de l'intensité délivrée par l'appareil.

Dispositif accessoires

Les bornes B9 et B10 sont prévues sur l'appareil pour la vérification de la tension de la pile étalon.

Disjoncteur de sécurité.

Un relais différentiel R1 dont une bobine est insérée dans le circuit de cathode de la lampe L3 et dont l'autre bobine est alimentée par un courant constant, est normalement au repos. Si le spot du galvanomètre s'écarte anormalement de sa position d'équilibre, le relais R1 vient au travail et coupe le contact X-Y.

Le relais R2 normalement au travail cesse d'être alimenté et la haute tension H.T.2 se trouve coupée, le contact I4 s'ouvrant; l'intensité dans la cellule tombe alors à zéro.

Un voyant lumineux V3 est alimenté lorsque le courant circule dans la cellule et s'éteint lorsque le relais R2 se déclanche.

Pour la mise en route, après que l'interrupteur général a été fermé, on enclanche le relais R2 en fermant le contact I2.

Le courant circule dans la cellule si tous les réglages sont corrects. Le contact I5 du relais R2 assure le verrouillage du relais R2 jusqu'au moment ou le relais R1 s'enclanche accidentellement ou jusqu'à ce qu'on ouvre le contact I6 prévu pour l'arrêt de l'appareil.

Un contact supplémentaire I3 du relais R2 ouvre le circuit du galvanomètre et de la pile étalon si le relais R2 est déclanché.

Chronomètre

L'électro-aimant de mise en marche d'un chronomètre peut être inséré entre les bornes B3 et B4. Le chronomètre démarre alors lorsque le starter est amené sur la position correspondant au passage du courant dans la cellule, grâce au contact I7 du starter. Si le relais R2 vient à se déclancher, il n'y a plus de tension aux bornes B3 et B4 et le chronomètre s'arrête.

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Cellule d'électrolyse

Le compartiment anodique est constitué par une large surface de mercure (50 cm^2) recouverte par une solution saturée de KCl. On pourrait remplacer cette surface de mercure par une surface d'argent. Le compartiment cathodique se compose d'un récipient contenant la solution à titrer et dans lequel plonge l'électrode de platine. Un agitateur électromagnétique assure l'agitation. Les deux compartiments sont reliés par une baguette filtrante remplie d'une solution saturée de KCl (Fig. 1). Ce montage évite, comme nous l'avons montré dans une précédente publication[7], la diffusion de produits d'oxydation anodique dans la solution à titrer: il n'y a donc aucune réduction parasite possible si l'on remarque que la réduction de l'oxygène dissous conduit elle-aussi à la disparition d'un H$^+$ par électron: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$.

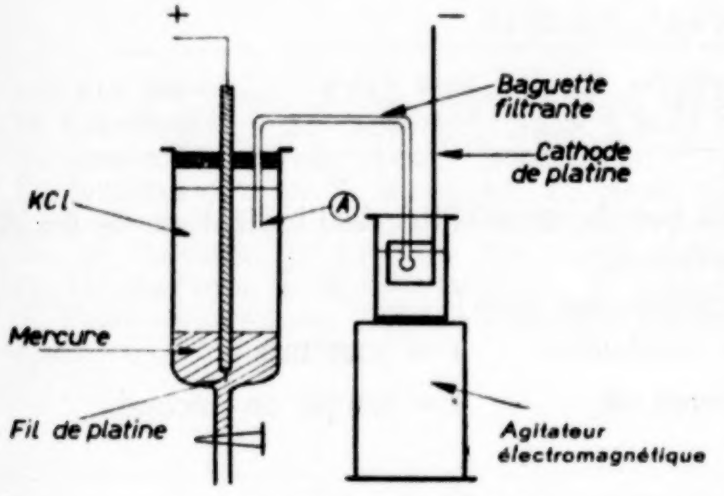

Fig. Cellule d'électrolyse

CHOIX DES CONDITIONS EXPÉRIMENTALES

Nous avons discuté ce choix dans une précédente publication[7]: nous utilisons l'intensité maximum compatible avec la plupart des dispositifs expérimentaux (70 à 100 mA). La durée du dosage est de 10 à 20 minutes pour des solutions d'acide $5 \cdot 10^{-2}$ N, le volume de la solution étant de 10 à 20 ml. Pour obtenir une neutralisation quantitative à 0.1% près et pour ne pas être gêné par le gaz carbonique de l'air, nous avons choisi le bleu de bromophénol comme indicateur de fin de réaction. Ce dernier permet d'arrêter l'électrolyse entre pH 4.3 et pH 4.8.

RÉSULTATS EXPÉRIMENTAUX

Nous avons dosé trois solutions différentes d'acide chlorhydrique. Les solutions (a) et (c) ont été étalonnées à partir de carbonate de sodium par deux expérimentateurs différents. La solution (b) a été titrée par une solution de soude elle-même étalonnée avec la solution d'acide.

Les tableaux suivants résument les expériences; les signent ≠ et o indiquent que les mesures ont été effectuées par deux expérimentateurs différents.

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	1 Solution (a)	Solution (b)		Solution (c)
	V = 10 ml	V = 10 ml	V = 25 ml	V = 10 ml
temps	9m 25s 6 ≠			
	9m 25s 5 ≠	12m 6s 1 0		12m 20s 5 0
	9m 26s 0 0	12m 6s 0 0	30m 14s 3 ≠	12m 22s 5 0
	9m 25s 3 0	12m 6s 8 0	30m 15s 5 ≠	12m 21s 8 0
	9m 27s 0 0			
moyenne du temps	9m 25s 9 565.9s ± 1.1	12m 6s 3 726.3s ± 0.5	30m 14s 9 1814.95 ± 0.1	12m 21s 6 741.6s ± 1.1

La précision du dosage est limité par la sensibilité de l'indicateur de fin de réaction (soit 2 sec dans le cas présent).

Calcul du titre en molécule grammes par litre:

$$c = \frac{i \times t}{F} \times \frac{1000}{V} \quad F = 96.500 \text{ coulombs} \quad i = 70.1 \text{ mA}$$

V = volume en ml

t = temps en seconde

titre	Coulométrie	Volumétrie	erreur
solution (a)	0.0411	0.04108	+0.07%
solution (b)	0.05276	0.05275	+0.02%
	0.05273	0.05275	−0.04%
solution (c)	0.05387	0.05375	+0.2 %

Les tableaux précédents montrent que les titres des acides sont exacts à 0.2% près.

La coulométrie à intensité constante permet donc d'étalonner une solution d'acide chlorhydrique à 0.2% près sans utiliser de substance de référence et assure ainsi un contrôle précieux du titre de solutions étalonnées par la volumétrie classique. La réalisation du dosage est simple grâce à l'emploi d'une alimentation à intensité constante et connue.

RÉSUMÉ

Nous fournissons description détaillée de l'alimentation à intensité constante que nous avons utilisé pour notre dosage coulométrique. Cette alimentation nous a permis de doser des solutions d'acide chlorhydrique $5 \cdot 10^{-2} N$ à 0.2% près en utilisant le bleu de bromophénol comme indicateur de fin de réaction.

SUMMARY

A detailed description is given of the supply of current at constant intensity that has been used for the coulometric determination. With this supply $5 \cdot 10^{-2} N$ hydrochloric acid solutions can be determined to within 0.2%, using bromphenol blue as indicator.

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ZUSAMMENFASSUNG

Wir gaben eine eingehende Beschreibung der Stromzuführung bei konstanter Stromstärke, die wir zu unserer coulometrischen Bestimmung benutzten. Diese Stromzuführung erlaubte uns unter Benutzung von Bromphenolblau als Indikator für den Endpunkt der Reaktion $5 \cdot 10^{-2} N$ Salzsäurelösungen mit einer Genauigkeit von 2% zu bestimmen.

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DAS ABGELEITETE POLAROGRAMM

von

H. L. KIES UND H. NIJON

Analytisch-chemisches Institut der Technischen Hochschule, Delft (Niederlande)

Es ist in gewissen Fällen zweckdienlich, abgeleitete Stromspannungskurven zu verwenden; die Höhe des Maximums gibt dann einen Massstab für die Konzentration.

HEYROVSKÝ[1,2] hat eine einfache Anordnung veröffentlicht, die von AIREY UND SMALES[3] beanstandet wurde. Es scheint nicht gut möglich, ohne Beeinträchtigung der Empfindlichkeit eine genügende Spannungsdifferenz zwischen den beiden Elektroden herzustellen; einige Versuche führten zu diesem gleichen Ergebnis.

Es erschien uns jedoch, dass die Verwendung eines Differentialgalvanometers* hier das gegebene Verfahren sei. Die Schaltung ist aus Abb. 1 ersichtlich. Der Kathodenstrom durchläuft nun gesondert eine der beiden Spulen des Galvanometers. Zur Reglung der Empfindlichkeit ist in jedem Zweig ein Ayrton-Nebenschluss („Shunt") vorgesehen. Die beiden Elektroden werden mit Hilfe des Mechanismus von AIREY UND SMALES[3] gleichzeitig abgetickt; das Gelenk ist jedoch stabiler ausgeführt. Die Verwendung des μ-Metalls erwies sich nicht als notwendig.

Der Ausschlag des Galvanometers zeigt die Differenz $i_2 - i_1$ an. Ein maximaler Ausschlag tritt auf, wenn:

$$\frac{d(i_2 - i_1)}{dE_1} = 0 \quad \ldots\ldots\ldots\ldots \quad (1)$$

Nun ist $E_1 = \pi_{an} - \pi_{c1} + i_1 r \quad \ldots\ldots\ldots\ldots \quad (2)$

und $E_2 = E_1 + \triangle E = \pi_{an} - \pi_{c2} + i_2 r \quad \ldots\ldots\ldots\ldots \quad (3)$

r ist die Summe der Widerstände einer einzigen Galvanometerspule mit ihrem Shunt und der Elektrolysenzelle.

Aus 2: $$\frac{dE_1}{di_1} = -\frac{d\pi_{c1}}{d\,i_1} + r = \left(\frac{1}{\varphi_0}\right)_1 + r = \left(\frac{1}{\varphi_m}\right)_1 \quad \ldots\ldots \quad (4)$$

Aus 3: $$\frac{dE_2}{di_2} = \frac{dE_1}{di_2} = -\frac{d\pi_{c2}}{d\,i_2} + r = \left(\frac{1}{\varphi_0}\right)_2 + r = \left(\frac{1}{\varphi_m}\right)_2 \quad \ldots\ldots \quad (5)$$

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* Fabrikat Kipp, Delft Nr. A 62.

Literatur S. 466.

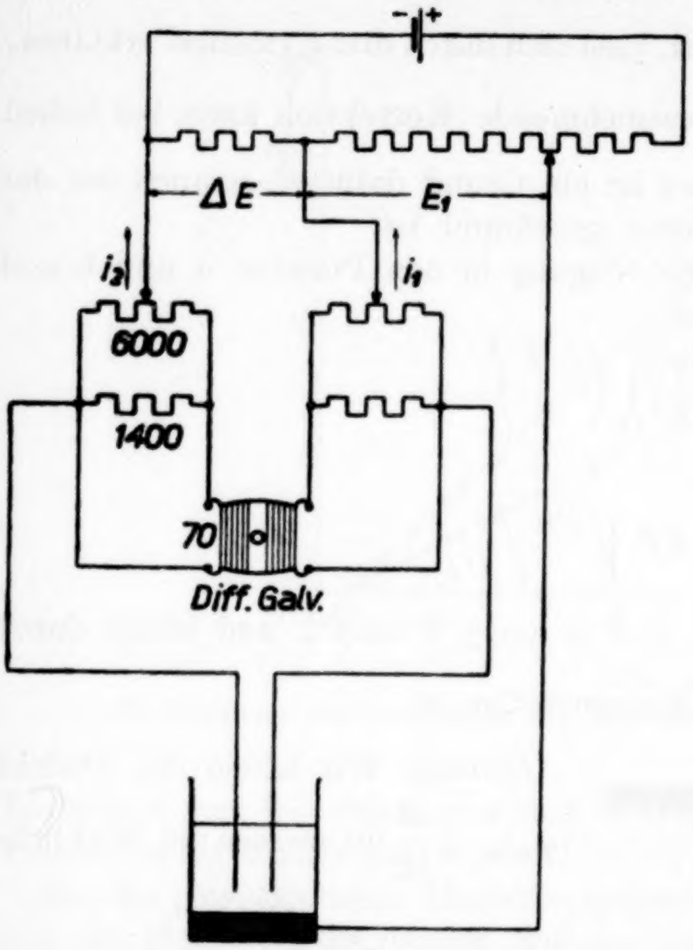

Abb. 1
Schaltung für ein Differentialpolarogramm.

In den vorhergehenden Gleichungen stellt φ_0 die Neigung im idealen Polarogramm ($r = 0$) und φ_m die wirkliche Neigung dar[4].

Aus (1), (4) und (5) folgt, dass im Maximum $(\varphi_m)_1 = (\varphi_m)_2$ und somit auch $(\varphi_0)_1 = (\varphi_0)_2$ ist.

Aus der Gleichung für das ideale Polarogramm folgt für

$$(\varphi_0)_1 = \frac{i_1(i_{d1} - i_1)}{i_{d1}} \cdot \frac{z_i \,.\, F_y}{R.T} \sqrt{\frac{D_R}{D_O}} \quad (6)$$

Wenn nun Sorge getragen wird, dass $i_{d1} = i_{d2} = i_d$, so ergibt sich aus (6) im Maximum $i_1 + i_2 = i_d$.

Dieser Zustand ist in Abb. 2 dargestellt.

Das Potential im Maximum differiert vom Halbwertpotential um einen Betrag $\frac{\triangle E + i_d r}{2}$; die Differenz gegenüber dem normalerweise gemessenen Halbwertpotential beträgt $\triangle E/2$: Abb. 3.

Der Wert φ_0 beim Halbstufen potential (zu bezeichnen mit $(\varphi_0)_{\frac{1}{2}}$) ist der Theorie gemäss proportional zu i_d, ist also auch der Konzentration proportional. Dass $i_2 - i_1$

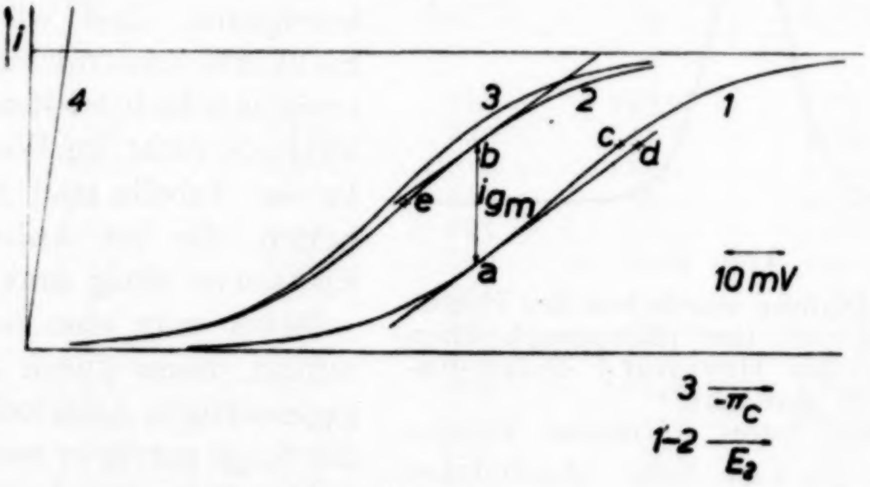

Abb. 2

Kurve 3	Ideales Polarogramm				
Kurve 4	Korrektionsausdruck	i	als Funktion von	$i.r$
Kurve 1	Wirkliches Polarogramm	i_2	als Funktion von	E_2
Kurve 2	,,	i_1	als Funktion von	E_2

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der Konzentration nicht proportional ist, lässt sich durch drei Ursachen erklären:

Erstens: $(\varphi_m)_{\frac{1}{2}} = \dfrac{(\varphi_0)_{\frac{1}{2}}}{1 + r(\varphi_0)_{\frac{1}{2}}}$. Die vorzunehmende Korrektion kann bei hohen Konzentrationen ±10% betragen. Dies ist ein Grund dafür, dass auch bei der Methode von VOGEL-RIHA[5] die Eichkurve gekrümmt ist.

Zweitens: Wir messen annähernd die Neigung in den Punkten *a* und *b* und nicht in *e*. Wir können nun schreiben:

$$(\varphi_m)_a = (\varphi_m)_{\frac{1}{2}} + \left(\frac{d\varphi_m}{dE}\right)_{\frac{1}{2}} \left(\frac{\triangle E}{2}\right) + \frac{1}{2}\left(\frac{d^2\varphi_m}{dE^2}\right)_{\frac{1}{2}} \left(\frac{\triangle E}{2}\right)^2$$

oder nach Auflösung:

$$(\varphi_m)_a = (\varphi_m)_{\frac{1}{2}} \left[1 - \frac{4R.T}{z_i.F_y} \left\{\frac{(\varphi_m)_{\frac{1}{2}}}{i_d}\right\}^3 (\triangle E)^2 \sqrt{D_O \Big/ D_R}\right]$$

Der Korrektionsfaktor beträgt für $\triangle E = 0.025$ V 11.5% und hängt durch den Faktor $\left\{\dfrac{(\varphi_m)_{\frac{1}{2}}}{i_d}\right\}^3$ wieder von der Konzentration ab.

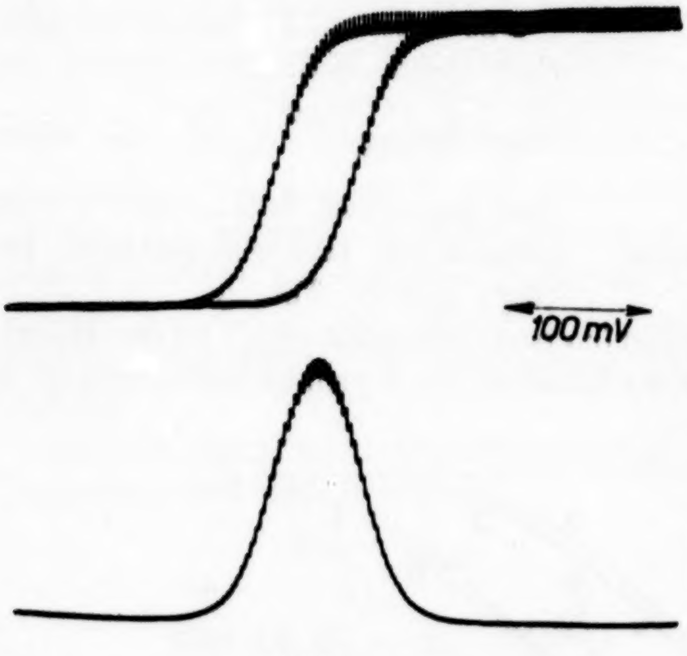

Abb. 3

Bei dieser Aufnahme wurde von der Potentiometerwalze und der photographischen Registrierung des Heyrovský Polarographen Gebrauch gemacht.
Empfindlichkeit beim normalen Polarogramm $G = \frac{1}{40}$ und beim abgeleiteten Polarogramm $G = \frac{1}{60}$.
$\triangle = 53$ mV
Konzentration 0.96 m.mol.$Pb(NO_3)_2$ pro Liter.
Als Anode fungierte das Bodenquecksilber.

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Drittens: Wir haben die Absicht $(\varphi_m)_a = \dfrac{\overline{ab}}{\overline{bd}}$ zu messen; in Wirklichkeit messen wir $\dfrac{\overline{ab}}{\overline{bc}} = \dfrac{i_g}{\triangle E}$.

Wie gross der Annäherungsfehler ist, lässt sich schwer berechnen.

Obenstehend ist dargelegt worden, dass es nicht auf einfache Weise möglich ist, die Messergebnisse so zu korrigieren, dass wir eine gerade Eichkurve konstruieren können. Dies braucht jedoch der Benutzung dieser Methode nicht im Wege zu stehen. In der Tabelle sind die Daten enthalten, die bei Aufzeichnung der Eichkurve nötig sind.

Bevor man eine Aufnahme vornimmt, muss durch Regelung der gegenseitigen Quecksilberhöhen dafür Sorge getragen werden, dass die beiden Diffusionsströme gleich sind. Diese Einstellung bildet einen Nachteil, der bei der VOGEL-RIHA Methode nicht vorkommt. Ferner gilt die

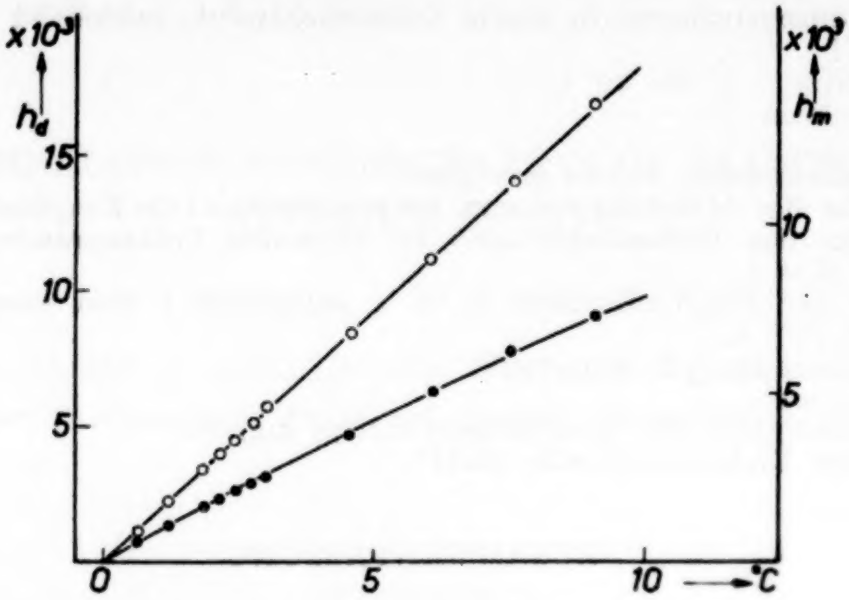

Abb. 4
Eichkurven des normalen (o) und des abgeleiteten (•) Polarogramms.

Eichkurve nur bei einem gewissen Werte des Kapillarfaktors, wie dies in der Polarographie immer der Fall ist.

Bei der angewendeten Umdrehungsgeschwindigkeit des Potentiometers lässt sich die Höhe des Maximums weniger genau messen als die Stufenhöhe eines gewöhnlichen Polarogramms. Diesem Übelstand kann evtl. dadurch abgeholfen werden, dass man die Umdrehungsgeschwindigkeit des Potentiometers herabsetzt.

TABELLE I

*C	h_m	$h_m/{*C}$	h_d	$h_d/{*C}$
9.07	7240	798	16850	1860
7.56	6200	820	14100	1860
6.05	4950	820	11150	1840
4.54	3730	822	8400	1850
3.02	2490	825	5640	1870
2.72	2280	838	5080	1870
2.42	2060	851	4470	1850
2.12	1800	849	3910	1845
1.82	1560	857	3390	1865
1.21	1050	868	2240	1850
0.605	519	856	1110	1840
0.242	208	860	451	1860
0.182	156	857	—	—
0.121	104	859	225	1860
0.0907	78	860	—	—
0.0605	53	876	113	1860
0.0242	21	868	—	—

Literatur S. 466.

Diverse Bleikonzentrationen in einem Grundelektrolyt, bestehend aus:

0.1*M* KCl)
0.2*M* KNO_3) bei 20° C
0.01% Gelatin)

**C*: Konzentration m.mol pro Liter
h_m: Höhe des Maximums in mm, umgerechnet auf die Empfindlichkeit $G = 1$.
h_d: Höhe des Diffusionsstromes im normalen Polarogramm, umgerechnet auf $G = 1$.
Bei der Empfindlichkeit $G = 1$ entspricht 1 mm einer Stromstärke $0.52 \cdot 10^{-9}$ A.

Angelegte Spannung $\triangle E = 0.0247$V.
Tropfzeit 3.32 sec.
Zufuhrgeschwindigkeit des Quecksilbers 0.1094 mg/sec.
Widerstand der Elektrolysenzelle 560Ω[6].

ZUSAMMENFASSUNG

Aufnahme eines abgeleiteten Polarogramms mit Hilfe eines Differentialgalvanometers.

Erklärung des nicht-linearen Verhältnisses zwischen der Konzentration und der Höhe des Maximums.

RÉSUMÉ

Enregistrement d'un polarogramme dérivé, à l'aide d'un galvanomètre différentiel.

Explication du rapport non linéaire entre la concentration et la hauteur du maximum.

SUMMARY

Registration of a derived polarogram by means of a differential galvanometer.

Explanation of the non-linear relation between concentration and height of the maximum.

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POLAROGRAPHIC DETERMINATION OF ALUMINUM IN TITANIUM ALLOYS

by

JAMES J. MIKULA AND MAURICE CODELL

Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa. (U.S.A.)

INTRODUCTION

Analytical methods based on the gravimetric precipitation of aluminum in titanium have been reported[18, 3]. These methods are based on a cupferron solvent extraction, after which aluminum is precipitated by use of ammonium hydroxide or 8-hydroxyquinoline. These methods, however, are limited to large amounts of aluminum and are not satisfactory for samples containing less than 0.2 per cent. This laboratory[2] has recently proposed a colorimetric method for the determination of aluminum based on the formation of a red lake using aluminon as the reagent after preliminary separation of titanium with cupferron. The method is applicable for concentrations between 0.01 and 0.40 per cent. aluminum.

This work was, therefore, undertaken in an attempt to develop a sensitive and accurate means of determining aluminum which would be applicable over a wide range.

The polarographic approach was pursued in an effort to develop a method of good sensitivity, reproducibility and relative freedom from interferences. PRAJZLER[15] made the first study of the polarographic behavior of aluminum. He studied the simultaneous estimation of iron, chromium and aluminum in a supporting electrolyte of $0.05N$ $BaCl_2$. The half wave potential is -1.75 versus S.C.E. which is so close to the discharge potential of sodium, potassium, or barium that the wave of aluminum is not fully developed when these ions are present in very large concentrations. Other investigators who determined aluminum polarographically in a weakly acid solution using a neutral salt as the electrolyte include: GULL[5] working with magnesium alloys, SEMERANO AND RONCHI[16], HÖVKER[6, 7] working with clays, FORD AND LEMAR[4] working with portland cement, and ALMEIDA[1] working with wine which had been stored in aluminum alloy containers. The success of all these methods, however, depends on a very rigid pH control. The solution to be polarographed must not have a pH less than about 3 because the aluminum wave will be masked by the hydrogen wave which precedes it. On the other hand, the pH must not be greater than the natural pH resulting from hydrolysis of aluminum ion, otherwise hydrous aluminum oxide will precipitate. Buffer solutions can not be used for regulating the pH, because the solution must not contain any weak acids. Weak acids can produce a large hydrogen wave which would obscure the aluminum wave completely. Because of the inherent disadvantages of pH control and difficulties experienced using inorganic salts as supporting electrolyte the above method of approach was abandoned.

An indirect procedure for aluminum was developed by Parks and Lykken[14]. Their method is based on the decrease in wave height of a 0.05 per cent. alcoholic solution of 8-quinolinol as a result of the precipitation of aluminum oxinate in an ammonia-ammonium chloride buffer of pH 9.8. A waiting period of 1 hour is necessary to secure a precipitation even 90 per cent complete. The quantitative determination of aluminum fluorometrically by using di-*o*-hydroxyazo dyes was developed by Weissler and White[19]. It is a known fact that the azo group yields a well-defined diffusion wave. Utilizing this knowledge Willard and Dean[20] developed an entirely new type of method for the polarographic determination of aluminum, based on the fact that the character of the polarogram of the dye is changed, due to the complexation of aluminum ion with di-*o*-hydroxyazo dyes. When aluminum ion is added in small concentrations to a solution containing an excess of the dye, a double wave is obtained. The first wave corresponds to the amount of unreacted dye, while the second wave is proportional to the complexed aluminum. The strongest point of this method lies in the fact that the reduction wave of the aluminum-dye complex occurs at a relatively positive potential, thereby permitting the use of buffers to control the pH which was not possible in the usual method for aluminum.

The principles established by Willard and Dean[20] for the polarographic determination of aluminum were used in the work reported here for determining aluminum in titanium alloys.

APPARATUS AND REAGENTS

A Sargent polarograph, Model XXI, was used in performing this work. Electrolysis was carried out in an H-type polarographic cell with a saturated calomel electrode[8, 9]. The cell was kept in a constant temperature water bath at 25.0° ± 0.1° C. Dissolved oxygen was removed by bubbling purified nitrogen through the solution for 10 minutes prior to the polarographic determination. The nitrogen was purified by passing it through vanadous sulfate solution[13].

The capillary used had m and t values of 1.99 mg per second and 3.69 seconds, respectively, which gave a capillary constant, $m^{2/3}t^{1/6}$, of 1.97 mg$^{2/3}$ sec$^{-1/2}$.

Standard Aluminum Solution No. 1 (1.00 ml = 0.100 mg aluminum) prepared by dissolving 1.760 grams of cp potassium aluminum sulfate crystals in water, adding 8 ml of 72 per cent. (12N) perchloric acid, and diluting to 1 liter.

References p. 475.

Standard Aluminum Solution No. 2. (1.00 ml = 0.010 mg aluminum) prepared by pipetting 50 ml of standard aluminum solution No. 1 into a 500 ml volumetric flask, adding 4 ml of perchloric acid (72 per cent.), and diluting to mark with water.

Ammonium acetate solution, 2*N*, prepared by dissolving 154 grams of the cp salt in water and diluting to 1 liter.

Eriochrome Violet BA (color index 169) 0.1 per cent. solution prepared by dissolving 1.00 gram of the dye in 1 liter of water.

Chloroform, analytical grade.

Hydrochloric acid, Sp. Gr. 1.19.

Nitric acid, Sp. Gr. 1.42.

Perchloric acid, 72 per cent.

Cupferron solution, 8 per cent. prepared by dissolving 4 grams of cupferron in 50 ml of water and filtering through No. 40 Whatman filter paper. Keep immersed in an ice bath until ready for use. This solution should be prepared fresh because it tends to decompose by heat and long standing.

Cupferron wash solution is prepared by adding 10 ml of cupferron solution (8 per cent.) to 500 ml of 10 per cent. hydrochloric acid. This solution should be kept in an ice bath until ready for use and should be freshly prepared.

Sodium hydroxide, 10 per cent. Dissolve 10 grams of cp sodium hydroxide in 100 ml of water.

Perchloric acid, 5*N*. Dilute 41.7 ml of perchloric acid (72 per cent.) to 100 ml with water.

EXPERIMENTAL

Titanium is reported by WILLARD AND DEAN[2] to be a serious interference in determining aluminum by complexation with di-*o*-hydroxyazo dyes. Therefore, the first problem to overcome was the complete removal of titanium. Precipitation with cupferron appeared to be the ideal means of achieving this end. Cupferron also offered the added advantage of removing many other ions which might be objectionable[10,17]. Since the cupferron precipitation is usually carried out in 1 to 9 sulfuric acid or hydrochloric acid solution, and sulfate-ions interfere in the polarographic determination of aluminum, hydrochloric acid was employed to dissolve the titanium alloys. Fortunately the 1 to 9 ratio of acid to water is not too critical in the precipitation, thus allowing moderate variations in acidity without affecting the complete removal of titanium. Precipitation was made from a cold solution to prevent the decomposition of cupferron.

Chloride ions which interfere if present in the final solution before polarographing, were removed by adding perchloric acid to the filtrate after removal of titanium and evaporating the sample to fumes. The sample was then in an ideal condition for completing the analysis. Any objectionable cations not removed by the cupferron were conveniently removed at this point by electrolysis with a mercury cathode [11,12]. The only cation remaining in solution at this point is essentially aluminum which was determined polarographically after being buffered with acetate at pH 4.6 and adding an excess of eriochrome violet BA dye.

Preparation of calibration curve

From a burette transfer into 50 ml volumetric flasks several representative size portions of standard aluminum solution covering the desired range of 0.01 to 0.50 mg of aluminum. Add about 10 ml of water to each flask, then 10 per cent sodium hydroxide dropwise until the solution becomes alkaline to methyl red. Add 5*N* perchloric acid until the solution becomes just acidic, then 1.00 ml of 5*N* perchloric acid in excess, plus 5 ml of 2.0*N* ammonium acetate. To the flasks containing less than 0.3 mg of aluminum add 10 ml of 0.1 per cent. Eriochrome violet BA solution; to those containing more than 0.3 mg of aluminum add 20 ml of 0.1 per cent. eriochrome violet BA. Dilute to the mark with water and mix. Immerse the flasks for 5 minutes in a water bath maintained at 55° to 70° C. Cool to room temperature under tap water and transfer a portion of the sample to a polarographic cell. Immerse the cell in a water bath maintained at 25° C. Bubble purified nitrogen through the sample solution for 10 minutes to remove dissolved oxygen. Polarograph the solution between -0.2 and -0.8 volt versus the saturated calomel electrode and measure the height of the second wave (Fig. 1).

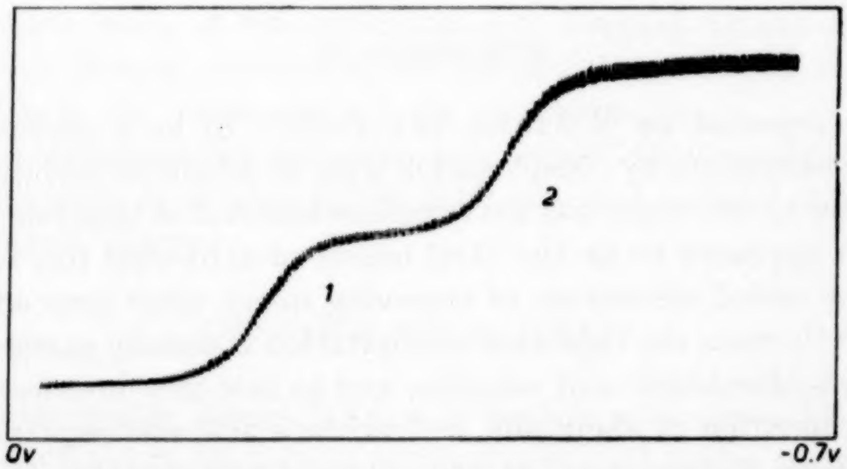

Fig. 1. Typical polarogram of solution containing aluminum and eriochrome violet BA buffered at pH 4.6
1. Excess unreacted dye
2. Aluminum-dye complex

To convert the wave height from millimeters to microamperes multiply by the sensitivity setting used in recording the polarogram. Plot the points on plain graph paper representing the current in microamperes as the ordinate and milligrams of aluminum as the abscissa. Draw a straight line through the points (Fig.2).

Procedure

A. For samples containing from 0.1 to 10 per cent. aluminum.

Dissolve 0.500 g of titanium contained in a 250 ml beaker with 30 ml of hydrochloric acid by warming on a hot plate. If the volume of acid is less than 25 ml after the titanium is completely dissolved, add enough hydrochloric acid to bring it up to that volume. Add 1 ml of nitric acid. After the titanium is oxidized, transfer the solution to a 100 ml volumetric flask, dilute to the mark with water and mix.

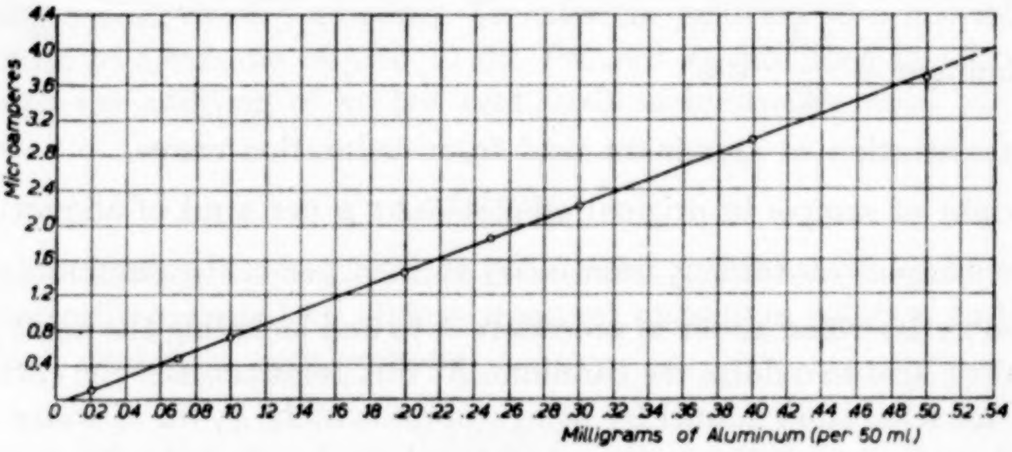

Fig. 2. Calibration curve for aluminum.

Transfer an aliquot of this solution (4.00 ml for samples containing 0.1 to 1.5 per cent. aluminum or 2.00 ml for samples containing 1.5 to 10 per cent. aluminum) into a 250 ml beaker, add 5 ml of hydrochloric acid and 45 ml of water. Place the beaker in an ice bath for about 10 minutes. Add 6 ml of freshly prepared cupferron solution and stir. Allow 2 minutes for the precipitate to coagulate and settle, then immediately filter through a No. 40 Whatman filter paper. Wash the beaker and precipitate several times with cold cupferron wash solution. Discard the precipitate. To the filtrate add 15 ml of nitric acid and 3 ml of perchloric acid. Place the sample on a hot plate and evaporate to fumes of perchloric acid. Fume the sample until the total volume of acid remaining is about 1 ml. Remove the sample from the hot plate and allow it to cool. Wash the cover and the sides of the beaker with a fine stream of water keeping the volume at a minimum. Add 10 per cent. sodium hydroxide solution until alkaline to methyl red then add 5*N* perchloric acid until the solution is just barely acid. For samples containing less than 3 per cent. aluminum add 1.00 ml of 5*N* perchloric acid, 5.0 ml of ammonium acetate, and 10 ml of eriochrome violet BA, then transfer the solution to a 50 ml volumetric flask and dilute to the mark. For samples containing more than 3 per cent. aluminum add 2.0 ml of 5*N* perchloric acid, 10 ml of ammonium acetate, and 30 ml of eriochrome violet BA, then transfer the sample to a 100 ml volumetric flask and dilute to the mark. Treat the samples

References p. 475.

as described in preparation of calibration curve beginning with the immersion of the flasks and contents for 5 minutes in a water bath maintained at 55° to 70° C. The concentration of aluminum present in the sample is read from the calibration curve (Fig. 2) which is prepared as described above.

When final volume of sample before polarographing is 50 ml

$$\%\ \text{aluminum} = \frac{A}{W} \cdot 100$$

When final volume of sample before polarographing is 100 ml

$$\%\ \text{aluminum} = \frac{2A}{W} \cdot 100$$

A = concentration of aluminum read from calibration curve.

W = weight of sample in original aliquot (0.01 g per 2 ml of aliquot)

B. For samples containing from 0.005 to 0.10 per cent. aluminum.

Proceed as described above in procedure A to and including the point of adding 1 ml of nitric acid to oxidize the titanium. At this point transfer the entire sample to a 250 ml separatory funnel by using approximately 45 ml of water. Add 100 ml of cold cupferron solution to the separatory funnel and shake for approximately 30 seconds to insure complete precipitation. Add 40 ml of chloroform, shake 30 seconds and allow the layers to separate, drain off and discard the bottom chloroform layer. Add an additional 40 ml of chloroform and repeat the extraction procedure with two or more 25 ml additions of chloroform until the chloroform and aqueous layers are both water white and clear. Drain off and discard the chloroform layer. To test for the complete removal of titanium add an additional 1 ml of cupferron to the aqueous layer. If a white flocculent precipitate forms at the point of contact between the solution and the excess reagent, the precipitation of titanium is complete. If a yellow precipitate appears upon the addition of the excess cupferron, continue adding cupferron until a white precipitate begins to form at the contact between the solution and the cupferron. A yellow precipitate indicates the presence of titanium and must be removed by additional chloroform extractions as described above until both layers appear water white and clear. Draw off and discard the chloroform layer, transfer the aqueous phase to a 400 ml beaker, add 15 ml of nitric acid and 3 ml of perchloric acid. Evaporate on a hot plate to fumes of perchloric acid and fume the sample until about 1 ml of acid remains. Continue as described in procedure A beginning at the point where the sample has been evaporated to fumes of perchloric acid.

C. For samples containing copper, cobalt, nickel or chromium.

These samples are treated exactly as described above in procedure A up to and including the fuming of the samples with perchloric acid. At this point the chromium is removed as volatile chromyl chloride by adding concentrated hydrochloric acid, 2 or 3 drops at a time, until the discharge of orange fumes ceases, thus indicating that practically all the chromium has been removed. Allow the sample to fume vigorously between each acid addition. If copper, cobalt, and nickel are absent, the sample may be diluted to about 10 ml and carried through the remainder of procedure A beginning with the addition of 10 per cent. sodium hydroxide until alkaline to methyl red. If copper, cobalt or nickel are present, transfer the sample to a 300 ml electrolysis beaker with water bringing the volume up to approximately 200 ml. Electrolyze the solution at a mercury cathode for 1 hour using a current of 5 amperes. Transfer the solution to a 400 ml beaker and evaporate to a volume of 5 to 10 ml. Proceed as described in procedure A starting with the addition of 10 per cent. sodium hydroxide until alkaline to methyl red.

RESULTS

The results shown in Table I indicate the accuracy of the method. The samples were synthetically prepared by adding standard aluminum solution to titanium sponge which contained no aluminum.

TABLE I

ANALYSIS OF TITANIUM METAL

Sample size mg	Final vol. ml	Aluminum added mg	Aluminum added %	Aluminum found % Average	Standard deviation	No. Determinations
400	50	0.02	0.005	0.0052	0.0008	6
400	50	0.28	0.070	0.072	0.0018	5
20	50	0.02	0.100	0.108	0.0027	7
20	50	0.09	0.450	0.464	0.0097	6
20	50	0.18	0.900	0.908	0.013	6
20	50	0.28	1.40	1.48	0.055	5
20	50	0.48	2.40	2.47	0.032	6
10	50	0.45	4.50	4.57	0.087	5
10	100	0.70	7.00	7.10	0.030	6
10	100	0.98	9.80	9.87	0.092	5

Interfering elements

Of the many elements which, according to WILLARD AND DEAN[20], must be absent in the final solution we need only be concerned with removing the following when dealing with aluminum determinations of commercial titanium alloys: Ti, V, Fe, Cu, Co, Ni and Cr. Titanium, vanadium and iron are completely removed by cupferron while copper is partially removed[9]. Chromium may be satisfactorily removed as chromyl chloride. Cobalt and nickel, plus any remaining Cu and Cr, may be removed by electrolysis at a mercury cathode[11,12].

Results showing the effectiveness of removing these elements are listed in Table II.

Alloys were prepared synthetically by adding the elements in the form of their soluble salts. 0.02 gram samples were used and the interfering elements were removed with a mercury cathode, except in the case of chromium which was removed as chromyl chloride.

TABLE II

ANALYSIS OF TITANIUM ALLOYS

Element added %	Aluminum added %	Aluminum found %
20 Chromium	1.00	0.97
20 Cobalt	1.00	1.04
20 Copper	1.00	1.03
20 Nickel	1.00	1.03
20 Iron	1.00	1.02

SUMMARY

Considerable interest has been shown in titanium metal because of its combination of desirable properties, including its favorable strength to weight ratio and its resistance to corrosion. Since titanium-aluminum alloys are fairly common, there is need for an accurate method of determining aluminum over a wide range of concentrations. This paper describes an accurate and fairly rapid polarographic method for determining aluminum based on the reduction of an aluminum-azo dye complex after removing titanium and other interferences by cupferron precipitation, followed by electrolysis at a mercury cathode when necessary. The reduction takes place at — 0.44 volt versus the saturated calomel electrode in a solution buffered at pH 4.6 with acetate. The method is sensitive from 0.01 mg to 0.50 mg of aluminum per 50 ml, covering a range of 0.005 to 10.0 per cent. aluminum.

RÉSUMÉ

Le titane présente un grand intérêt en raison de ses alliages à propriétés variées (densité favorable et résistance à la corrosion). Les alliages titane — aluminium étant très courants, une méthode précise de dosage de l'aluminium (sur une grande échelle) est nécessaire. Les auteurs décrivent une méthode polarographique, précise et rapide, pour doser l'aluminium; elle est basée sur la réduction du complexe aluminium — colorant azo, après élimination du titane et d'autres éléments gênants par précipitation au moyen de cupferron, suivie d'une électrolyse avec cathode de mercure si nécessaire. La réduction s'effectue à — 0.44 volt, électrode au calomel saturée, solution tampon pH 4.6 à l'acétate. La méthode est sensible pour des teneurs en aluminium de 0.50 mg/50 ml (0.005 à 10.0 % Al).

ZUSAMMENFASSUNG

Ein beträchtliches Interesse wurde dem Titanmetall wegen seiner Kombination von wünschenswerten Eigenschaften, einschliesslich seiner günstigen Festigheit im Vergleiche zum Gewichts- und seiner Korrosionswiderstandfähigkeit, entgegengebracht. Da Titan-Aluminium-Legierungen ziemlich üblich sind besteht Bedarf für eine genaue Bestimmungsmethode für Aluminium in einem weiten Konzentrationsbereich. In dieser Arbeit wird eine genaue und ziemlich schnelle polarographische Methode zur Bestimmung von Aluminium beschrieben, die sich auf die Reduktion

eines Aluminium-Azofarbstoffkomplexes gründet, nach der Entfernung von Titan und anderen störenden Ionen durch Ausfällung mit Cupferron und darauf, wenn nötig, durch Elektrolyse an einer Quecksilberkathode. Die Reduktion findet bei — 0.44 Volt gegen gesättigte Kalomelelektrode in einer mit Acetat gepufferten Lösung bei pH 4.6 statt. Die Methode ist von 0.01 mg bis 0.50 mg Aluminium pro 50 ml empfindlich und deckt einen Bereich von 0.005 — 10.0% Aluminium.

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DÉTERMINATION POLAROGRAPHIQUE INDIRECTE DE SULFATE

par

OTTO ALCIDES OHLWEILER

Escola de Engenharia, Porto Alegre, sous l'auspice du Conselho Nacional de Pesquizas (Brésil)

Lorsqu'une substance n'est pas électroactive, son dosage polarographique indirect est possible dans certains cas. Une des manières de conduire la détermination consiste à isoler la substance à doser avec un réactif précipitant électroactif, puis à dissoudre convenablement le précipité et polarographier la solution. Par exemple, SOUCHAY[1], étudiant la polarographie des periodates, a suggéré, pour la détermination indirecte du potassium, la précipitation préalable du métal alcalin comme periodate. HORTON ET THOMASON[2] ont proposé une méthode pour la détermination de l'anion sulfurique, basée sur la réduction de celui-ci en hydrogène sulfuré, l'absorption du gaz en solution ammoniacale de chlorure de cadmium, la dissolution du sulfure de cadmium et la mesure du courant de diffusion du cadmium dans la solution résultante. La méthode de TOCKSTEIN ET ŠĚRÁK[3], pour la détermination du soufre, consiste à le séparer sous forme de sulfate de baryum, qui est alors dissous dans une solution ammoniacale d'ions argent libres et un excès d'argent complexé avec l'acide éthylènediaminotétracétique. Ce mélange polarographié, présente deux ondes, la première due aux ions argent et la seconde à l'argent complexé. La dissolution du sulfate de baryum s'opère avec formation du complexe correspondant de baryum, plus stable que celui d'argent, et la libération d'une quantité équivalente d'argent, qui augmente la première onde polarographique (plus positive). Dans toutes les méthodes citées, il faut recueillir de petites quantités de précipité, ce qui est peu avantageux. MONNIER ET BESSO[4] ont proposé une méthode polarographique pour la détermination indirecte du potassium. Elle est basée sur la diminution de l'onde polarographique de la dipicrylamine avant et après l'addition du potassium à une solution de dipicrylaminate de sodium ($10^{-2}M$) saturée de dipicrylaminate de potassium à 20° C. La méthode exige une attente de 12 heures pour avoir une précipitation quantitative du dipicrylaminate de potassium. Il faut tracer les courbes étalons chaque fois qu'un nouveau réactif est mis en usage ou lorsque le réactif a souffert de variations de température.

Le but du présent travail est d'étudier une autre possibilité de détermination

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indirecte d'ions non électroactifs ou d'ions électroactifs lorsque la détermination directe présente des difficultés. Il s'agit d'établir un état d'équilibre parfaitement défini entre la solution contenant l'ion désiré et un sel peu soluble, constitué d'un ion électroactif capable de former des ondes polarographiques bien marquées.

Principe de la méthode. Quand une solution contenant un ion du type B^{-m} est agitée avec un sel peu soluble du type A_mB_n, il s'établit finalement un état d'équilibre donné par l'équation suivante:

$$A_mB_n \rightleftharpoons mA^{+n} + nB^{-m}. \; . \; . \; . \; . \; . \; . \; . \; . \; . \; .$$

D'accord avec le principe du produit de solubilité, le système est réglé par l'expression:

$$S_{A_mB_n} = f_A^m [A^{+n}]^m \, . \, f_B^n [B^{-m}]^n. \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

L'équilibre s'établit moyennant le passage, pour la solution, d'une partie du sel peu soluble A_mB_n. Si la concentration de la solution originale (B^{-m}) est égale à b molaire et si nous supposons que la portion dissoute du sel A_mB_n donne une concentration x du cation A^{+n} dans la solution on a alors :

$$S_{A_mB_n} = f_A^m x^m \, . \, f_B^n \left(b + \frac{nx}{m}\right) . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

La dernière équation montre que la concentration du cation A^{+n} dans la solution finale dépend de la concentration de la solution originale en relation avec l'anion B^{-m} et des valeurs des coefficients d'activité des ions qui font partie du système. L'état final d'équilibre peut être parfaitement caractérisé par la concentration du cation A^{+n} dans la solution. Dans ces conditions, si l'anion B^{-m} est une substance non électroactive et le cation A^{+n} capable de donner une onde polarographique bien définie, alors l'anion B^{-m} pourra être déterminé indirectement par la mesure du courant de diffusion du cation électroactif A^{+n}. Il est clair que pour cela il faut satisfaire certaines conditions:

a) La solubilité du sel auxiliaire doit être telle que l'ion électroactif passe en solution, en concentrations comprises dans les limites imposées par l'analyse polarographique.

b) Les équilibres doivent être établis dans des milieux de force ionique bien déterminée, car les valeurs des coefficients d'activité des ions doivent rester approximativement constantes.

c) La température doit être parfaitement déterminée (le produit de solubilité du sel auxiliaire variant avec la température).

Le cas pratique étudié dans le présent travail est la détermination indirecte de sulfate au moyen de sulfate de plomb comme sel auxiliaire. Quand on agite une solution, contenant des ions sulfuriques avec du sulfate de plomb solide, il

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s'établit, finalement, un état d'équilibre capable d'être caractérisé par la concentration en ion plomb acquise par la solution. L'équation générale (2) appliquée au cas en question prend la forme suivante :

$$S_{PbSO_4} = f_{Pb^{+2}}(x) \cdot f_{SO_4^{-2}}(b + x) \quad \ldots\ldots\ldots\ldots \quad (3)$$

Des résultats approximatifs peuvent être obtenus si l'on applique l'équation simplifiée :

$$x(b + x) = s^2, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

dans laquelle s est la solubilité du sulfate de plomb dans le milieu considéré. L'équation peut être écrite sous la forme suivante:

$$x^2 + bx - s^2 = 0.$$

La solution générale d'une équation de ce type nous est donnée par

$$x = -b/2 \pm \sqrt{(b/2)^2 + s^2}\,; \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

la racine négative peut être négligée, une valeur négative de x n'ayant pas de sens physique.

Par conséquent, il est possible de calculer approximativement la concentration en ions plomb que va acquérir la solution, après avoir atteint l'état d'équilibre, si l'on connaît la concentration en sulfate dans la solution originale et la solubilité du sulfate de plomb dans la même solution. Il est vrai que les courbes plomb-sulfate, obtenues d'après l'équation (5) diffèrent considérablement de celles tracées à partir de données entièrement expérimentales (Figs. 2, 3, 4 et 5), mais elles peuvent donner une idée générale sur l'équilibre SO_4^{-2}-$Pb^{+2}/PbSO_4$.

L'étude expérimentale du système SO_4^{-2}-$Pb^{+2}/PbSO_4$ a été effectuée en vue de la détermination polarographique indirecte des sulfates. L'utilisation de ce système pour la détermination polarographique indirecte des sulfates, exigeant l'usage de solutions de force ionique pratiquement constante, l'étude de l'équilibre SO_4^{-2}-$Pb^{+2}/PbSO_4$ fut faite en relation avec des solutions contenant des électrolytes capables d'opérer comme électrolytes indifférents dans la mesure du courant de diffusion du plomb (par exemple: le nitrate de potassium, le chlorure de potassium, l'acide nitrique et l'acide chlorhydrique). Dans la pratique, l'addition de tels électrolytes, en quantité convenable et plusieurs fois supérieure à celle correspondant à la concentration originale des solutions à étudier, permet de maintenir la force ionique pratiquement constante.

Dans la première partie du travail expérimental, ont été étudiées les conditions d'équilibre du système (principalement les effets des variations de concentration saline et de température), ont été également tracées plusieurs courbes plomb-sulfate d'après les données expérimentales et vérifiée la reproductibilité du système. Des essais polarographiques ont servi à établir les conditions générales de travail lors de la détermination indirecte de sulfates et la précision de la méthode.

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ÉTUDE DU SYSTÈME SO_4^{-2}-Pb^{+2}/$PbSO_4$

Dans l'étude expérimentale du système SO_4^{-2}-Pb^{+2}/$PbSO_4$, les solutions contenant un sulfate en concentrations variables et l'électrolyte indifférent en concentrations bien définies, sont agitées avec du sulfate de plomb durant un temps suffisant pour établir l'état d'équilibre. Finalement, les solutions sont soumises au dosage du plomb. La méthode utilisée dans la détermination du plomb consiste à le précipiter et le peser sous forme de chromate de plomb.

Réactifs et appareils. a) Sulfate de plomb. Le sulfate de plomb finement divisé est préparé par mélange rapide des solutions de nitrate de plomb et de sulfate de sodium. Le précipité est filtré et lavé à l'eau.

b) Sulfate de potassium 0.01*M*. 1.743 g de sulfate de potassium séché par chauffage au rouge sombre sont dissous dans l'eau et dilués à 1 litre.

c) Nitrate de potassium 1*M*. 101.1 g du sel séché sont dissous dans l'eau et dilués à 1 litre.

d) Chlorure de potassium 1*M*. 74.6 g du sel séché sont dissous dans l'eau et dilués à 1 litre.

e) Acide nitrique 1 et 0.05*M*. La solution molaire est préparée à partir du réactif concentré par dilution jusqu'à la densité correspondante. La solution 0.05*M* est obtenue par dilution de la solution molaire.

f) Acide chlorhydrique 1 et 0.05*M*. La solution molaire est préparée à partir du réactif concentré par dilution jusqu'à la densité correspondante. La solution 0.05*M* est obtenue par dilution de la solution molaire.

g) Agitateur mécanique Sargent-74065, permettant de faire des essais en série (base capable de supporter jusqu'à sept flacons de 250 ml).

Procédé. Des volumes convenables de solutions de sulfate de potassium 0.01*M* et d'électrolytes indifférents sont mesurés et transvasés dans des fioles jaugées de 250 ml et dilués jusqu'au trait de jauge. Les solutions obtenues sont transférées dans des flacons rodés de 250 ml, traitées avec 0.5 g de sulfate de plomb, agitées pendant trente minutes et, finalement, filtrées à travers papier filtre (S & S, no 589, bande rouge, 9 cm), les deux premières portions de liquides filtrés sont abandonnées. On prélève 200 ml de filtrat et on y dose le plomb par la méthode au chromate.

Toutes ces opérations, jusqu'à la mesure de la solution pour la détermination du plomb, sont effectuées en série, à une température déterminée. Plusieurs essais préliminaires ont montré qu'en travaillant dans les conditions décrites, le temps indiqué de trente minutes d'agitation est suffisant pour que l'état d'équilibre soit atteint.

Solubilité du sulfate de plomb. Il est intéressant de connaître la solubilité du sulfate de plomb dans les solutions d'électrolytes déjà cités et les effets qu' exercent sur elle les variations de concentration des électrolytes et de température.

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TABLE I

SOLUBILITÉ DU SULFATE DE PLOMB DANS LES SOLUTIONS DE QUELQUES ELECTROLYTES À DIVERSES CONCENTRATIONS (mole/litre × 10^4).

Electrolyte	Température (°C)	Concentration de l'électrolyte (mole/litre)			
		0.025	0.050	0.075	0.100
KNO_3-HNO_3 0.005*M**	17	2.16	2.72	3.24	3.67
KCl-HCl 0.005*M**	22	2.58	3.44	4.30	5.04
HNO_3	17	2.61	3.69	4.67	5.64
HCl	17	2.95	4.52	6.14	7.79

* Les solutions de nitrate de potassium et de chlorure de potassium renferment les acides respectifs dans la concentration indiquée, afin d'éviter les éventuels effets d'hydrolyse du cation plomb.

La Table I donne une série de solubilités du sulfate de plomb dans les solutions de quelques électrolytes, à diverses concentrations. Ces valeurs se trouvent représentées graphiquement dans la Fig. 1. La solubilité est plus grande dans les solutions acides en raison de la formation des ions HSO_4^-. D'autre part, la solubilité est plus grande dans les solutions chlorhydriques que dans les nitriques;

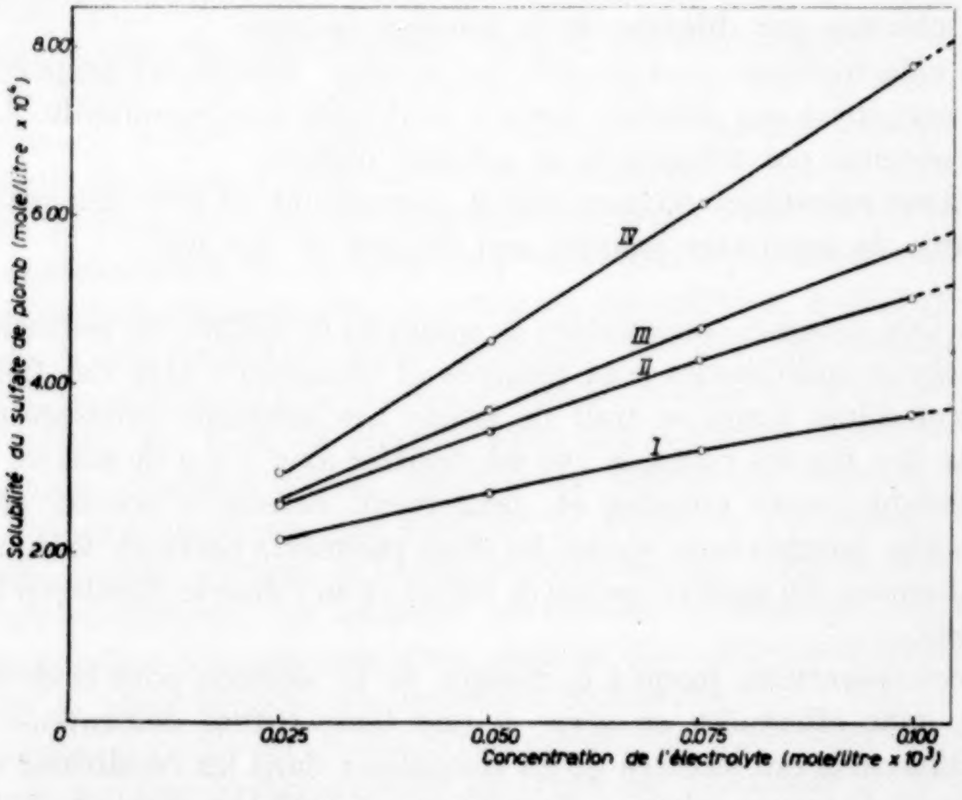

Fig. 1. — Courbes de solubilité du sulfate de plomb en solutions dans quelques électrolytes.
I — Courbe correspondant aux solutions de KNO_3-HNO_3 0.005*M*;
II — Courbe correspondant aux solutions de KCl-HCl 0.005*M*;
III — Courbe correspondant aux solutions de HNO_3;
IV — Courbe correspondant aux solutions de HCl.

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de même elle est plus grande dans les solutions de chlorure de potassium que dans celles de nitrate de potassium, à cause de la tendance de l'ion Pb^{+2} à former l'ion complexe $PbCl^-$.

Les courbes de solubilité n'étant pas parfaitement rectilignes, la solubilité du sulfate de plomb ne varie pas uniformément avec la concentration des électrolytes. La table II donne l'effet de la variation de concentration de l'électrolyte sur la solubilité du sulfate de plomb, calculé comme valeur moyenne entre les concentrations 0.095 et 0.105*M* pour une différence de concentration égale à 0.001 *M*. On voit, cependant, que les coefficients de concentration augmentent dans l'ordre suivant des électrolytes : nitrate de potassium, chlorure de potassium, acide nitrique et acide chlorhydrique.

TABLE II

EFFET DE LA VARIATION DE CONCENTRATION DE L'ÉLECTROLYTE SUR LA SOLUBILITÉ DU SULFATE DE PLOMB

Electrolyte	Coefficient de concentration
KNO_3 0.1*M*—HNO_3 0.005*M*	0.46%
KCl 0.1*M*—HCl 0.005*M*	0.51%
HNO_3 0.1*M*	0.64%
HCl 0.1*M*	0.81%

L'effet de la température est montré par la Table III. Le coefficient de température par degré centigrade, calculé en relation avec la solubilité du sulfate de plomb à 25° C, augmente dans l'ordre suivant des électrolytes : nitrate de potassium, chlorure de potassium, acide nitrique et acide chlorhydrique.

TABLE III

EFFET DE LA TEMPÉRATURE SUR LA SOLUBILITÉ DU SULFATE DE PLOMB

Electrolyte	Température (° C)	Solubilité (mole/litre $\times 10^4$)	Coefficient de température par degré centigrade*
KNO_3 0.1*M*—HNO_3 0.005*M*	15	3.60	
	28.5	4.13	0.98%
KCl 0.1*M*—HCl 0.005*M*	17	4.74	
	28	5.46	1.22%
HNO_3 0.1*M*	17	5.64	
	28	6.66	1.46%
HCl 0.1*M*	18.5	7.89	
	27	9.29	1.82%

* Calculé en relation avec la solubilité du sulfate de plomb à 25° C.

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L'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$. Les Figs. 2, 3, 4 et 5 représentent une série de courbes plomb-sulfate relatives à l'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$, en des milieux divers. En ordonnées, sont données les concentrations de plomb des solutions en équilibre en fonction des concentrations en sulfate des solutions originales. Les courbes

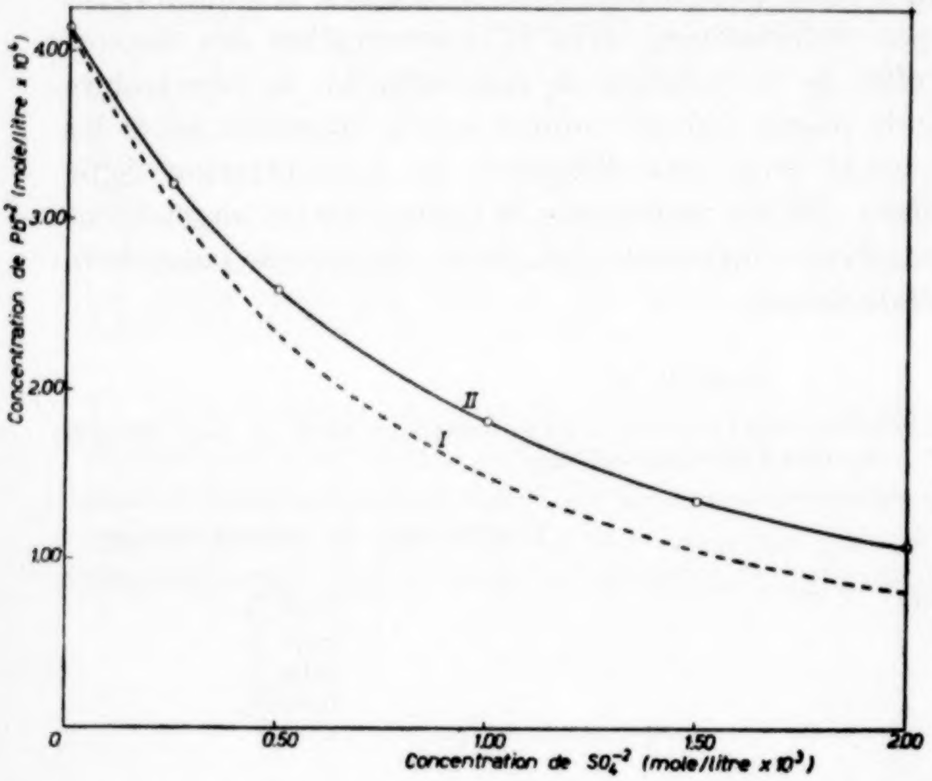

Fig 2. — L'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ en KNO_3 0.1*M*—HNO_3 0.005M.
I — Courbe calculée (t = 28.5° C);
II — Courbe tracée avec données expérimentales (t = 28.5° C).

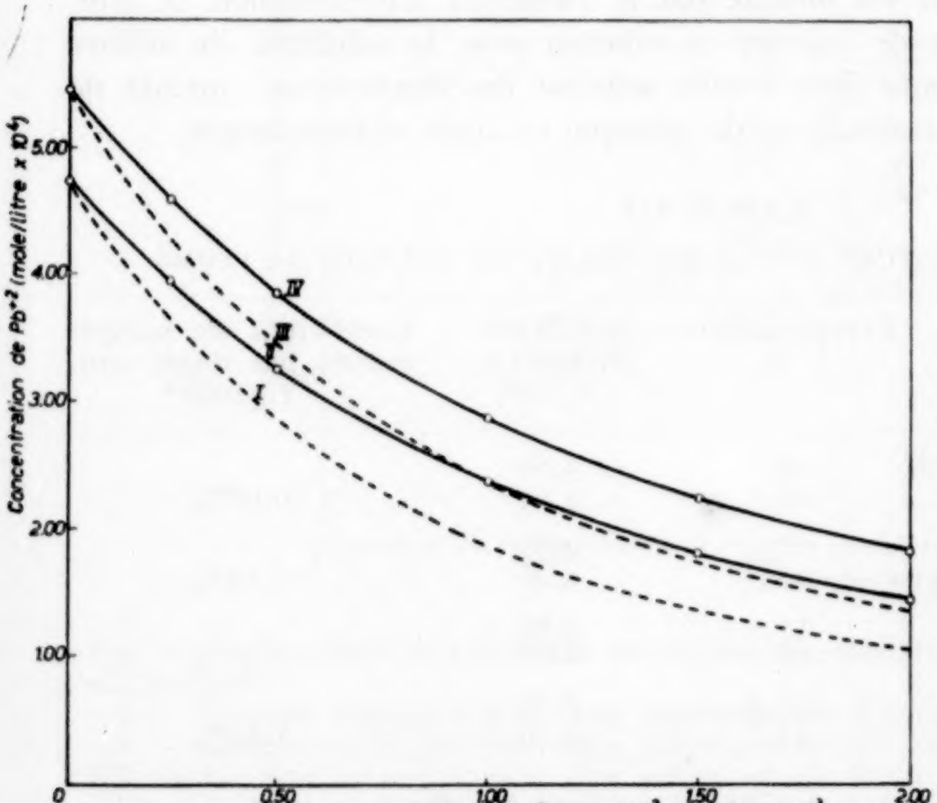

Fig. 3. — L'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ en KCl 0.1*M*—HCl 0.005*M*.
I — Courbe calculée (t = 17° C);
II — Courbe tracée avec données expérimentales (t = 17° C);
III — Courbe calculée (t = 28° c);
IV — Courbe tracée avec données expérimentales (t = 28° C).

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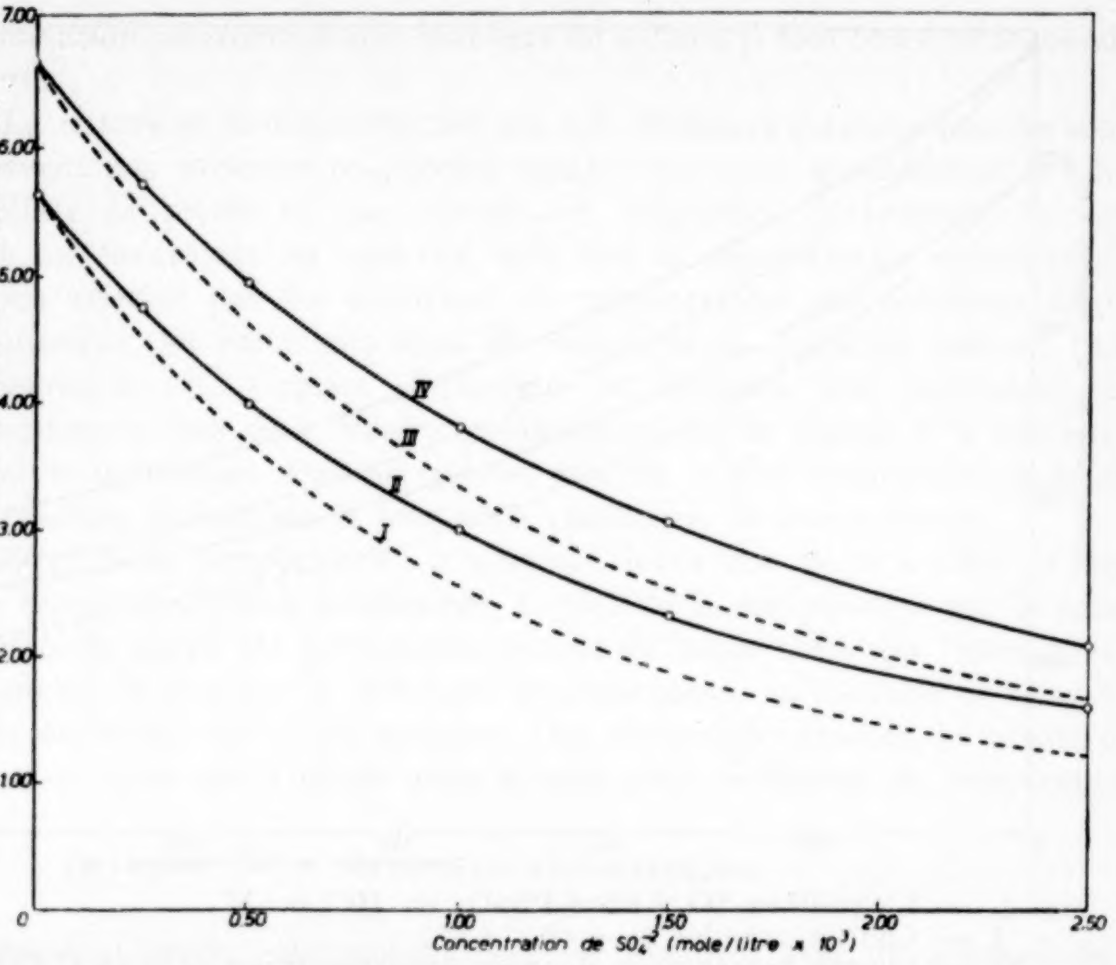

Fig. 4. — L'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ en HNO_3 0.1*M*.
I — Courbe calculée ($t = 17°$ C);
II — Courbe tracée avec données expérimentales ($t = 17$°C);
III — Courbe calculée ($t = 28°$ C);
IV — Courbe tracée avec données expérimentales ($t = 28°$ C).

tracées sont en fonction de la solubilité du sulfate de plomb, par rapport au milieu considéré, moyennant l'application de l'équation (5), tandis que toutes les autres sont tracées sur la base de données entièrement expérimentales.

Afin d'établir le temps d'agitation nécessaire pour que le système atteigne l'état d'équilibre, il a été effectué une série d'essais consistant à agiter les solutions de sulfate de potassium $2.5 \cdot 10^{-4}M$ dans HNO_3 0.1*M*, à la température de 20° C, durant des temps divers:

Essai	Temps d'agitation	Concentration de Pb^{+2} (mole/litre $\times$ 10⁴)
1	15 minutes	4.87
2	30 ,,	5.02
3	45 ,,	4.98
4	60 ,,	5.02

Une autre série d'essais, effectués dans les mêmes conditions (ci-dessus indiquées), mais tous avec un temps égal d'agitation (le temps nécessaire pour que le

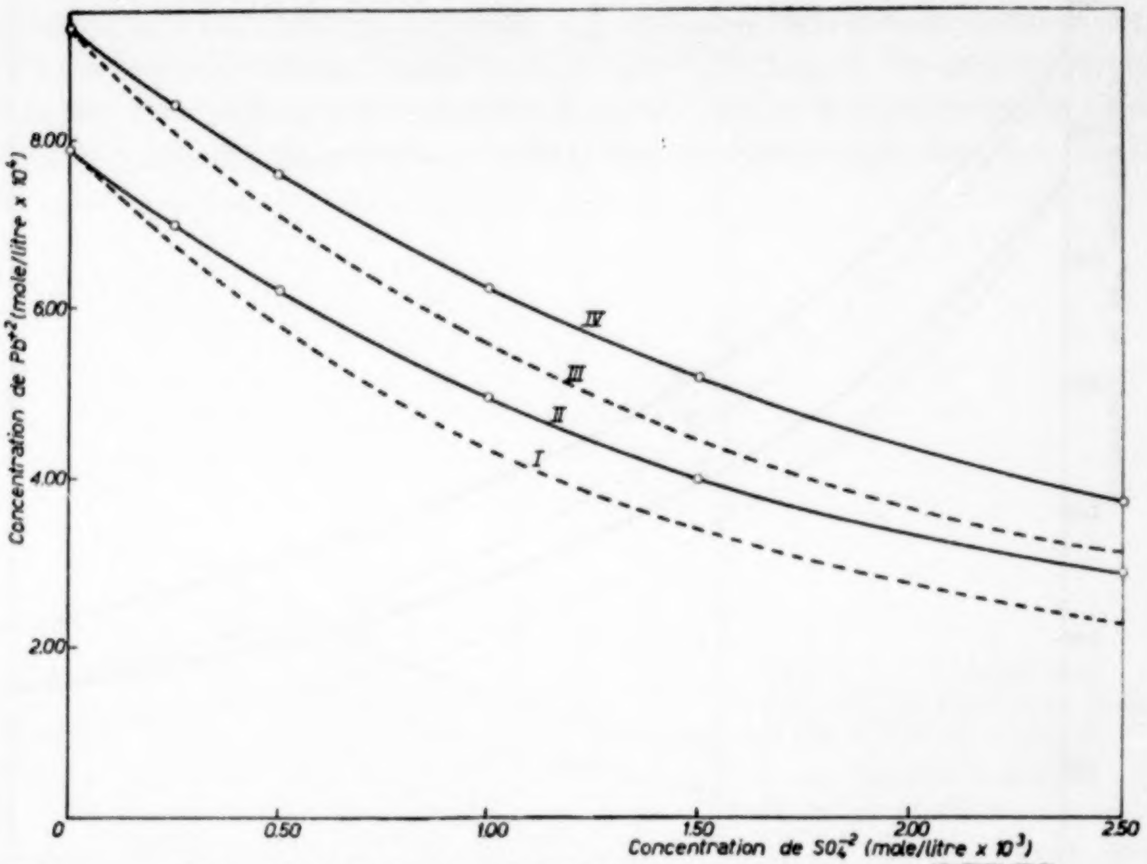

Fig. 5. — L'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ en HCl 0.1*M*.
I — Courbe calculée (t = 18.5° C);
II — Courbe tracée avec données expérimentales (t = 18.5° C);
III — Courbe calculée (t = 27° C);
IV — Courbe tracée avec données expérimentales (t = 27° C).

système entre en équilibre, c'est-à-dire, 30 minutes) a été réalisé en vue de vérifier la reproductibilité du système. Les résultats sont les suivants :

Essai	1	2	3	4	5
Concentration de Pb^{+2} (mole/litre × 10^4)	4.98	5.02	5.00	4.98	5.02

En conséquence, d'après la moyenne des valeurs trouvées, qui est égale à 5.00, les déviations maximums observées ne sont pas supérieures à 0.4%; l'écart normal est égal à 0.02. Il est possible que la reproductibilité du système soit encore plus grande, la grandeur des déviations observées correspondant à l'ordre de précision de la méthode utilisée pour la détermination du plomb.

Conclusions. L'étude expérimentale effectuée nous montre que les solutions de sulfate, agitées avec du sulfate de plomb, entrent rapidement en équilibre. L'équilibre peut être caractérisé par la concentration en plomb dans la solution résultante. La reproductibilité du système est très satisfaisante. Seule la première partie des courbes plomb-sulfate présente des variations satisfaisantes de la concentration de plomb pour les variations de concentrations de sulfate.

Pour que l'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ puisse être utilisé comme base pour la détermination polarographique indirecte du sulfate, il faut observer les conditions suivantes :

a) La nature et la concentration des sels étrangers présents dans les solutions ne doivent pas varier en proportion capable d'affecter sensiblement la solubilité du sulfate de plomb et, par conséquent, l'équilibre du système. Souvent, on ajoute un électrolyte en quantité telle que la concentration saline résultante soit peu affectée par les variations de concentration des solutions originales. Pratiquement, les variations dans la concentration saline ne doivent pas être supérieures à 1%. Comme électrolyte, on utilisera une substance capable de fonctionner, lors de la mesure polarographique du plomb, à la manière d'un électrolyte indifférent. Des électrolytes étudiés, le plus intéressant est le nitrate de potassium, présentant le plus petit coefficient de concentration.

b) Effet de la température : le système devra être porté à l'état d'équilibre à une température bien déterminée. L'effet de la température sur la solubilité du sulfate de plomb est approximativement du même ordre que l'effet de la température sur le courant de diffusion. Pratiquement, un contrôle de température de plus ou moins 0.5° C est suffisant. Des électrolytes étudiés, le nitrate de potassium est celui qui a révélé aussi le plus petit coefficient de température.

ÉTUDE POLAROGRAPHIQUE

Appareil. L'étude polarographique a été exécutée avec un appareil du type Heyrovský, de la firme allemande Leybold, avec capillaire du même fabricant; temps de formation de goutte égal à 2.2 secondes; hauteur de la colonne de mercure : 60 cm. Cellule : type Heyrovský.

Données expérimentales. L'étude polarographique de l'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ a été développée en vue de l'établissement des conditions de travail mieux adaptées à la détermination indirecte du sulfate. Il a été aussi effectué des essais pour vérifier la précision des déterminations polarographiques.

a) Les premiers essais polarograhiques ont été conduits d'après le procédé suivant :

100 ml de solution contenant le sulfate, en concentration connue, et un électrolyte, en concentration convenable, sont agités avec environ 0.2 g de sulfate de plomb, à une température bien déterminée, durant 30 minutes. La solution résultante est filtrée à travers un papier (S & S, no. 589, bande rouge, 9 cm); les deux premiers filtrats sont abandonnés. 50 ml du filtrat sont transvasés dans la cellule et traités avec 2.5 ml d'hydroxyde de sodium 1*N* contenant 0.5 g de sulfite de sodium et 2 gouttes de rouge de méthyle 0.1%. Finalement, la solution est polarographiée, avec une sensibilité de 1/30.

Les résultats trouvés concordent avec les données des courbes plomb-sulfate dans la précision des mesures polarographiques. Afin de vérifier la précision de ce procédé, il a été effectué deux séries d'essais avec des solutions de sulfate,

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respectivement, $2.5 \cdot 10^{-4}$ et $1.5 \cdot 10^{-3} M$ dans KNO_3 $0.1 M$ — HNO_3 $0.005 M$, à la température de 25° C. Les résultats trouvés sont donnés dans la Table IV.

TABLE IV

ESSAIS SUR LA REPRODUCTIBILITÉ

Concentration de sulfate (mole/litre)	Essai	Hauteur de l'onde du plomb (mm)	Ecart
$2.5 \cdot 10^{-4} M$	1	53.9	0.2
	2	53.5	0.2
	3	53.6	0.1
	4	53.8	0.1
	5	53.9	0.2
	Moyenne :	53.7	Ecart normal : 0.19
$1.5 \cdot 10^{-3} M$	1	21.2	0.1
	2	21.1	0.2
	3	21.5	0.2
	4	21.4	0.1
	5	21.2	0.1
	Moyenne :	21.3	Ecart normal : 0.17

Ces valeurs donnent une idée de la précision avec laquelle est mesurée l'onde du plomb. Il est intéressant de connaître l'effet de l'erreur commise dans la mesure du courant de diffusion du plomb, dans la détermination indirecte du sulfate. L'effet peut être calculé graphiquement d'après la courbe plomb-sulfate de la Fig. 2. Le calcul montre que dans le 95% des cas, l'erreur relative, dans la détermination indirecte du sulfate, est inférieure aux valeurs ci-dessous :

Concentration de sulfate	$10^{-4} M$	$2.5 \cdot 10^{-4} M$	$5 \cdot 10^{-4} M$	$10^{-3} M$	$1.5 \cdot 10^{-3} M$
Erreur relative	5.6%	3.3%	2.6%	2.1%	2.1%

b) En dernier lieu, il a été réalisé une série d'essais polarographiques pour vérifier la possibilité d'établir l'équilibre du système SO_4^{-2}-Pb^{+2}/$PbSO_4$, dans la cellule polarographique même, par le passage d'un courant d'hydrogène à travers la solution. Pour cela 20 ml d'une solution de sulfate de potassium $2 \cdot 10^{-4} M$ en KCl 0.1 M — HCl 0.005 M, contenant 0.02% de gélatine, sont traités successivement avec 0.1 g de sulfate de plomb et agités, par un courant d'hydrogène, pendant des temps croissants (t = 25° C). Ensuite, les solutions sont directement polarographiées, avec une sensibilité égale à 1/50.

Les résultats trouvés sont les suivants :

Essai	Temps de passage du gaz (minutes)	Hauteur de l'onde du plomb (mm)
1	10	40.5
2	20	43.5
3	20	43.5
4	30	43.2
5	30	43.5

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D'après ces résultats on voit que 20 minutes de passage du gaz sont suffisantes pour porter la solution à l'état d'équilibre. De plus, les quatre derniers résultats montrent une reproductibilité du même ordre que celle trouvée avec les essais antérieurs.

Cette dernière méthode présente les avantages suivants: a) l'équilibre est établi dans la cellule polarographique même ; b) il n'est pas nécessaire de filtrer la solution.

Conclusions. L'étude de l'équilibre SO_4^{-2}-Pb^{+2}/$PbSO_4$ montre qu'il peut servir de base pour la détermination polarographique indirecte de sulfates, lorsque sont obtenues les conditions déjà signalées, concernant la concentration saline du milieu et le contrôle de la température. La nécessité de travailler avec des solutions de concentration saline pratiquement constante constitue, certainement, une restriction de la méthode. Le contrôle de la température dans les limites pointées est courant dans les déterminations polarographiques. Dans les applications possibles, actuellement en étude, on envisage les déterminations de sulfate dans les eaux traitées, de sulfate dans les sels (nitrates et chlorures alcalins) et de soufre dans les fers et aciers.

RÉSUMÉ

Il a été étudié le système SO_4^{-2}-Pb^{+2}/$PbSO_4$ en vue de son utilisation pour la détermination polarographique indirecte du sulfate. Une solution renfermant le sulfate, dans des conditions bien définies de force ionique et de température, agitée avec du sulfate de plomb, conduit à un état d'équilibre capable d'être caractérisé par la concentration de plomb dans la solution finale. Il a été étudié les effets de variations de concentration saline du milieu et de température. Les essais de détermination indirecte du sulfate, par mesure polarographique du plomb, ont donné des résultats parfaitement satisfaisants au point de vue de la précision. Dans les applications possibles, présentement en étude, l'auteur cite les déterminations de sulfate dans les eaux traitées et dans les sels, et de soufre dans les fers et aciers.

SUMMARY

The system SO_4^{-2}-Pb^{+2}/$PbSO_4$ was studied from the point of view of its indirect polarographic determination of sulfate. A solution containing sulfate, under well-defined conditions of ionic force and temperature, when agitated with lead sulfate, leads to an equilibrium state that may be characterized by the lead concentration in the solution. The effects of the saline concentration and of temperature variations were studied. The experiments of indirect determination of sulfate, based in polarographic measurement of the lead, have given satisfactory results concerning accuracy. Among the possible applications, the author cites the determination of sulfate in treated water, in salts and in iron and steel.

ZUSAMMENFASSUNG

Zwecks Anwendung zur indirekten polarographischen Sulfatbestimmung wurde das System SO_4^{-2}-Pb^{+2}/$PbSO_4$ untersucht. Schüttelt man eine Sulfat enthaltende Lösung unter wohldefinierten Versuchsbedingungen bezüglich ionischer Kraft und Temperatur mit Bleisulfat, so wird ein Gleichgewichszustand erreicht, welcher durch die Konzentration des Bleis in der Endlösung charakteristiert werden kann.

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Der Einfluss der Salzkonzentrationsänderungen im Medium und die Einwirkung der Temperaturschwankungen wurden untersucht. Die Versuche zur indirekten Sulfatbestimmung durch die polarographische Bleibestimmung waren hinsichtlich der Genauigkeit vollkommen zufriedenstellend. Unter den Anwendungsmöglichkeiten, welche augenblicklich noch untersucht werden, mögen die Sulfatbestimmung in Wasser, wie sie in den Wasserwerken üblich ist, und die in Salzen, ferner die Schwefelbestimmung in Eisen und Stahl genannt werden.

BIBLIOGRAPHIE

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[3] A. Tockstein and L. Šerák, travail présenté au Congrès de Polarographie Pratique, Bratislava, 1952, et résumé en *Anal. Chem.*, 24 (1952) 914.

[4] D. Monnier and Z. Besso, *Anal. Chim. Acta*, 7 (1952) 380.

Reçu le 18 mai 1953

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

PROGRAMME OF MEETINGS FOR THE SESSION 1953-54

including meetings of the Local Sections and Subject Groups of the Society

ORDINARY MEETINGS OF THE SOCIETY

Wednesday, October 7th, 1953, at 7 p.m.
Symposium on *Destruction of Organic Matter*. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Friday, October 23rd, 1953, at 5 p.m.
Organised by the Physical Methods Group of the Society. Subject: *Paper Electrophoresis*. Southampton University. Afternoon visit to Esso Refinery at Fawley.

Wednesday, November 4th, 1953, at 7 p.m.
Meeting for reading of Original Papers. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Wednesday, December 2nd, at 7 p.m.
Lecture by Professor C. H. GRAY, M.D., D.Sc., F.R.C.P., F.R.I.C., on *Recent Advances in Medical Chemistry*. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Friday, January 29th, 1954, at 7 p.m.
Organised by the Microchemistry Group of the Society.
Sir John Cass College, Jewry Street, London, E.C.3. Exhibition of apparatus during the afternoon and evening.

Wednesday, April 7th, 1954.
Organised by the Biological Methods Group of the Society. Subject: *The Comparison of Chemical and Biological Estimation of Drugs in Quantitative Pharmacology*. Meeting in London.

Wednesday, May 5th, 1954, at 7 p.m.
Meeting for reading of Original Papers. Meeting Room of the Chemical Society, Burlington House, London, W.1.

ANNUAL GENERAL MEETING

(held in the Meeting Room of the Royal Society, Burlington House, London, W.1.)

Friday, March 5th, 1954, at 4.30 p.m.
followed at 5 p.m. by The Bernard Dyer Memorial Lecture given by E. B. HUGHES, D.Sc., F.R.I.C.

NORTH OF ENGLAND SECTION

Hon. Secretary: Arnold Lees, F.R.I.C., 87 Marshside Road, Southport, Lancs.

Saturday, September 26th, 1953, at 2.30 p.m.
Joint Symposium with the Microchemistry Group and the Liverpool and North-Western Section of the Royal Institute of Chemistry on The Training and Education of Microchemists. Mayor's Parlour, Town Hall, Southport. Visits to Simpson's

Gold Thread Works, Preston, on *Friday afternoon, September 25th,* and to Victoria Colliery, Standish, nr. Wigan, and Southport Gas Works on *Saturday morning.*

Saturday, November 28th, 1953, at 2 p.m.

Meeting on *Chromatography.* Speaker: Dr. R. L. M. SYNGE, F.R.S. City Laboratories, Liverpool.

Saturday, January 30th, 1954, at 2 p.m.

Annual General Meeting, followed by an Ordinary Meeting, at which the President, Dr. D. W. KENT-JONES, F.R.I.C., will present a Paper. Engineer's Club, Manchester.

Saturday, April 10th, 1954, at 2 p.m.

Discussion. City Laboratories, Liverpool.

SCOTTISH SECTION

Hon. Secretary: J. A. Eggleston, B.Sc., A.R.I.C., Boots Pure Drug. Co., Ltd., Motherwell Street, Airdrie, Lanarkshire.

Tuesday, November 10th, 1953, at 7.15 p.m.

Ordinary Meeting. Central Station Hotel, Glasgow.

Wednesday, December 16th, 1953, at 7.30 p.m.

Joint Meeting with the Stirlingshire and District Sections of the Society of Chemical Industry and the Royal Institute of Chemistry on *Principles of Chromatography,* by Dr. R. L. M. SYNGE, F.R.S., Lea Park Restaurant, Callendar Road, Falkirk.

Wednesday, January 20th, 1954, at 12.45 p.m.

Annual General Meeting. Rhul Restaurant, 123 Sauchiehall Street, Glasgow, C.2.

A Meeting on *Infra-red Spectroscopy* is planned for the Spring of 1954 at Edinburgh.

MICROCHEMISTRY GROUP

Hon. Secretary: D. F. Philips, A.R.I.C., 101 South Promenade, St. Annes-on-Sea, Lytham St. Annes, Lancs.

Saturday, September 26th, 1953, at 2.30 p.m.

Joint Symposium with the North of England Section and the Liverpool and North-Western Section of the Royal Institute of Chemistry on *The Training and Education of Microchemists.* Mayor's Parlour, Town Hall, Southport.

Visits to Simpson's Gold Thread Works, Preston, on *Friday afternoon, September 25th,* and to Victoria Colliery, Standish, nr. Wigan, and Southport Gas Works on *Saturday morning.*

Friday, January 29th, 1954, at 6.45 p.m.

Annual General Meeting, followed at 7 p.m. by an Ordinary Meeting of the Society organised by the Microchemistry Group. Sir John Cass College, Jewry Street, London, E.C.3. Exhibition of apparatus during the afternoon and evening.

Friday, May 7th, 1954, at 7.45 p.m.

Joint Meeting with the London Section of the Royal Institute of Chemistry on *Microchemical Methods in Biochemistry.* Zoological Lecture Theatre, The University, Reading. Afternoon visit to be arranged.

PHYSICAL METHODS GROUP

Hon. Secretary: R.A.C. Isbell, A. Inst. P., Hilger & Watts, Ltd., Hilger Division, 98 St. Pancras Way, London, N.W.I.

Friday, October 23rd, 1953, at 5 p.m.

Ordinary Meeting of the Society organised by the Physical Methods Group. Subject: *Paper Electrophoresis.* Southampton University. Afternoon visit to Esso Refinery at Fawley.

Tuesday, November 24th, 1953, at 6 p.m.

Annual General Meeting, followed at 6.30 p.m. by a Lecture by the retiring Chairman, Dr. J. HASLAM, F.R.I.C. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Tuesday, February 9th, 1954, at 6.30 p.m.
Meeting on *Coulometric Analysis*. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Tuesday, March 9th, 1954, at 6.30 p.m.
Meeting on *Refractometry and Interferometry*. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Tuesday, April 6th, at 6.30 p.m.
Meeting on *Mass Spectrometry*. Meeting Room of the Chemical Society, Burlington House, London, W.1.

Friday, May 28th, 1954.
Meeting on *Fluorimetry*. Seascale, Cumberland. Afternoon visit to be arranged.

POLAROGRAPHIC DISCUSSION PANEL

Hon. Secretary: G. W. C. Milner, B.Sc., F.R.I.C., A. Inst. P. Building 148, A.E.R.E. Harwell, Nr. Didcot, Berks.
The Annual General Meeting of the Panel is planned for November, 1953.

BIOLOGICAL METHODS GROUP

Hon. Secretary: S. A. Price, B.Sc., Walton Oaks Experimental Station, Vitamins, Ltd., Dorking Road, Tadworth, Surrey

Friday, October 2nd, 1953, at 10.30 a.m. to 5 p.m.
Joint Symposium with the Crop Protection Panel of the Agriculture Group, S.C.I., the Association of Applied Biologists and the Pharmacological Society on *Organo-phosphorus Insecticides*. Large Chemistry Lecture Theatre, Imperial College, London, S.W.7.

Friday, December 11th, 1953, 2.30 p.m. to 7 p.m.
Joint Symposium with the Pharmaceutical Society on *The Estimation of Pyrogenic Activity*.

Annual General Meeting of the Biological Methods Group at 4.10 p.m. Place to be arranged.

Wednesday, April 7th, 1954.
Ordinary Meeting of the Society in two sessions, organised by the Biological Methods Group, on *Comparison of Chemical and Biological Estimation of Drugs in Quantitative Pharmacology*. Meeting in London.

Guests introduced by Members are welcome at the Scientific Meetings

Registered office of the Society: 7-8 Idol Lane, London, E.C.3. Telephone: MANsion House 6608.

REVUE DE LIVRES

Massanalyse I et II, Gerhart Jander et Karl Friedrich Jahr, sixième édition. W. de Gruyter & Co, Berlin, 1952.

Nous n'avons pas à présenter la collection allemande ,,Göschen" qui a offert, depuis le début de ce siècle, maints ouvrages remarquables aux chimistes et aux physiciens.

Cette fois l'éditeur de la collection, Walter de Gruyter, nous envoie un traité de volumétrie, en deux brochures, intitulé ,,Massanalyse". Les deux tomes, forts de 140 pages chacun, traitent des bases théoriques et pratiques de l'analyse quantitative. Les descriptions des analyses sont développées avec suffisamment de détails pour faire de cet ouvrage un traité pratique de laboratoire, mais la partie théorique n'y est pas négligée pour autant. On est heureux de constater que chaque méthode et même chaque analyse est introduite théoriquement. De ce fait cet ouvrage n'est pas seulement pratique, mais aussi didactique.

Le premier tome décrit les appareils utilisés en volumétrie, la préparation précise des solutions titrées (entre autres, un chapitre précieux sur l'étalonnage des ballons jaugés) et toutes les méthodes d'oxydo-réduction. Enfin la théorie de la neutralisation, le pH, les indicateurs, etc.

Le deuxième tome aborde l'acidi-alcalimétrie, les méthodes par précipitation, formation de complexes et un chapitre sur la conductométrie: Dosages par mesures de conductibilité ou par potentiométrie. Là encore la partie théorique est remarquablement bien expliquée.

Nous pouvons recommander, sans aucune restriction, cet ouvrage très dense et pratique ... jusqu'à son format (de poche: 11 × 15.5 cm). Il rendra service au praticien, en lui décrivant un nombre considérable d'analyses, mais surtout à l'étudiant qui appréciera sa clarté et son caractère didactique.

P. Zwahlen (Genève)

DOSAGE DU POTASSIUM À L'AIDE D'UN RÉACTIF AU COBALTINITRITE DE LITHIUM

par

MME THÉRÈSE DUPUIS

Laboratoire de Recherches micro-analytiques de l'Ecole Nationale Supérieure de Chimie, Paris (France)

On sait que les méthodes de dosage du potassium à l'aide du cobaltinitrite de sodium ne sont pas satisfaisantes à cause de la composition variable du précipité, représentée par le schéma $[Co(NO_2)_6]$ $(K,Na)_3.nH_2O$. On a donc cherché à remplacer le sodium par un autre métal alcalin ne présentant pas l'inconvénient de précipiter en même temps que le potassium en proportions non définies. Le choix s'est porté sur le lithium dont l'ion a des dimensions assez différentes de celui du potassium; leurs rayons atomiques sont en effet pour Li: 0.60 A, pour K: 1.33 A. On s'est inspiré pour cela de ce qui se passe dans le cas du césium précipité par le cobaltinitrite de sodium et qui fournit un précipité de composition constante $[Co(NO_2)_6]Cs_3.H_2O$.

Les essais effectués avec une solution fraîche de cobaltinitrite de lithium ont confirmé cette hypothèse. Le précipité jaune obtenu, analogue à celui de sodium-potassium est quantitatif et ne contient pas de lithium. Examiné au microscope il se présente sous forme de cubes jaunes clairs.

La composition du réactif utilisé se rapproche de celle de celui de TYSDALL employé pour le dosage du césium et qui conduit, comme nous l'avons vérifié à des résultats très satisfaisants. Elle est la suivante:

Solution 1: 1.5 g de nitrate de cobalt — amener à 14 ml avec de l'eau — ajouter 0.6 ml d'acide acétique pur.

Solution 2: 2.7 g de nitrite de lithium en solution dans 9 ml d'eau. Cette composition correspond au rapport: sel de $Co/LiNO_2/CH_3COOH = 1/2.5/1$. 20 ml de ce réactif sont nécessaires pour 0.1 g de ClK. Les deux solutions sont mélangées dans un petit barboteur et l'excès de vapeurs nitreuses est enlevé par passage d'air à l'aide d'une trompe à vide pendant 2 heures environ. Le réactif doit être utilisé immédiatement ou au plus dans la journée.

Les liquides de lavage utilisés sont l'acide acétique à 10%, l'alcool éthylique ou méthylique et l'éther.

ANALYSE QUANTITATIVE

Gravimétrie

Afin d'établir une méthode gravimétrique, on a préparé une quinzaine de précipités à partir de prises d'essais différentes dont la teneur en potassium variait de 2 à 50 mg. Ces précipités ont été filtrés soit sur creuset de verre fritté G_3 ou G_4, soit sur creuset de verre garni d'une pastille de soie de verre de 0.4 cm environ d'épaisseur. On les lave quatre fois avec l'acide acétique à 10% puis une fois avec l'alcool, une fois avec l'éther et on les sèche dans un courant d'air.

L'examen des liquides de lavage recueillis séparément montre que six lavages suffisent pour éliminer l'excès du réactif, et qu'il ne s'y trouve pas de potassium provenant d'une dissolution partielle du précipité.

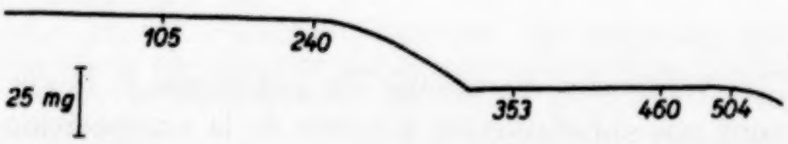

Fig. 1. Courbe de thermolyse du cobaltinitrite de potassium.

L'enregistrement des courbes de thermolyse (Fig. 1), des précipités ainsi préparés montre qu'en chauffage linéairement croissant de 300°/h et pour une quantité de potassium inférieure à 20 mg le produit étudié garde un poids constant jusqu'à 220° environ. Puis on constate un départ global d'eau et de vapeurs nitreuses jusqu'à 300° où s'amorce un deuxième palier horizontal; le produit correspondant est stable jusqu'à 460° au moins.

L'examen de ces deux paliers montre qu'ils peuvent tous deux servir pour la gravimétrie. Le précipité séché à 105-110° ainsi que le produit noir obtenu le long du palier entre 300 et 460° ont été analysés. La composition du premier correspond a $Co/NO_2/K = 1/6/3$ soit à la formule $[Co(NO_2)_6]K_3.2H_2O$. La précipitation a été effectuée à des températures variant entre 25 et 55°. Le produit séché à l'étuve à 110° est hygroscopique et il faut le peser en vase fermé dans le cas des pesées sur la microbalance.

Le deuxième palier correspond à la composition ($CoO + 3NO_3K$) établie en dosant le cobalt, le nitrate et le potassium et confirmée sur les courbes de thermolyse par le poids obtenu après chauffage à 400°.

Dans le cas où la couche de précipité est épaisse, c'est-à-dire, quand la quantité de potassium mise en jeu est supérieure à 20 mg, un crochet à 300° suivi d'une lente remontée dans la courbe indique une réoxydation lente du nitrite résiduel en nitrate. On retrouve en effet cette trace de nitrite à l'analyse qualitative du résidu laissé à 300°. Dans ce cas, le palier qui correspond à la composition ($CoO + 3NO_3K$) est moins étendu et la pesée sous forme de cobaltinitrite à $2H_2O$ est préférable.

Pour des prises d'essai contenant de 5 à 20 mg de potassium, on peut utiliser les deux formes de pesée. Les facteurs analytiques sont de 0.240 pour le cobaltinitrite à $2H_2O$ et 0.310 pour le mélange $CoO + 3NO_3K$. Dans l'ensemble, les résultats sont toujours légèrement élevés.

Avec le réactif indiqué, les ions Ba^{+2}, Sr^{+2}, Ca^{+2} et Na^+ ne donnent lieu à aucune précipitation contrairement à Mg^{+2}, NH_4^+, Rb^+ et Cs^+. Toutefois, on le suppose, le dépôt du potassium ne peut avoir lieu en présence de sodium comme on le voit sur les exemples suivants:

avec K: 11, 6 mg et Na: 6 mg, l'erreur sur le potassium est +6%

avec K: 2, 1 mg et Na: 2 mg, l'erreur atteint 20%.

Dans le Tableau I on a comparé les résultats fournis par les deux formes de pesée pour des quantités comprises entre 4 et 52 mg de potassium.

TABLEAU I

GRAVIMÉTRIE

FACTEURS ANALYTIQUES: POUR LE COBALTINITRITE À $2H_2O$: 0.240
POUR $CoO + 3NO_3K$: 0.310

K Calculé en mg	Pesée en cobaltinitrite à $2H_2O$ Trouvé en mg	erreur p. 100	Pesée en $CoO + 3NO_3K$ Trouvé en mg	erreur p. 100
52.4	53.16	+ 1.3	53.2	+ 1.5
45.9	46.68	+ 1.6	46.09	+ 0.4
20.95	21.1	+ 0.75	21.08	+ 0.65
27.98	28.8	+ 2.5	28.2	+ 0.61
23.3	23.5	+ 0.8		
21.1	21.36	+ 0.9		
20.3	20.4	+ 0.5		
11.66	11.73	+ 0.6	11.69	+ 0.3
11.66	11.61	− 0.4	11.62	− 0.3
11.66	11.67	+ 0.1	11.50	− 1.4
7.12	7.15	+ 0.4	7.18	+ 0.8
4.19	4.3	+ 2.5	4.29	+ 2.2

L'erreur moyenne pour ces teneurs vaut 0.7%.

En conclusion, la précipitation du potassium par le cobaltinitrite de lithium permet la pesée d'un précipité de composition $[Co(NO_2)_6]K_3.2H_2O$ exempt de lithium ou celle d'un mélange $CoO + 3NO_3K$. Les résultats peuvent être obtenus à 0.7% près à condition d'opérer la précipitation avec un réactif préparé depuis moins de 24 heures.

Titrimétrie

Le précipité de cobaltinitrite de potassium possédant une composition constante doit se prêter à un dosage d'oxydo-réduction des groupements NO_2 par le permanganate. Les résultats sont satisfaisants à condition d'admettre que trois atomes de potassium correspondent à douze équivalents au lieu de onze comme on devrait s'y attendre puisque le cobalt est trivalent dans les cobaltinitrites.

Pour le traitement du précipité en vue de la manganimétrie, deux modes opératoires ont été essayés, l'un en microtube de centrifugeuse et l'autre en microbécher et baguette filtrante à soie de verre.

Dans le premier cas, le précipité est lavé en aspirant le liquide surnageant après centrifugation à l'aide d'un tube effilé et recourbé vers le haut. Il est pratiquement impossible d'éviter la présence de traces de précipité à la surface du liquide et la seconde méthode nous a paru préférable. Elle est en même temps plus rapide.

Le mode opératoire utilisé est le suivant: Le précipité préparé comme dans le paragraphe précédent est lavé très soigneusement avec l'acide acétique à 10% par aspiration à l'aide d'une microbaguette de verre de 3 cm de haut garnie d'un tampon de soie de verre (quelques mg) jusqu'à élimination totale du réactif au nitrite. Le liquide aspiré doit être incolore. Le dernier lavage se fait avec quelques gouttes d'eau et les dernières gouttes de liquide sont aspirées de façon à éliminer le plus possible l'acide acétique.

Le précipité est alors attaqué par le permanganate $0.02N$ et l'acide sulfurique à 20%. Le bécher peut être chauffé au bain-marie à 60° *au maximum* pour favoriser la dissolution et l'oxydation des groupements nitrites. La liqueur est transvasée dans une petite fiole à dosage avec la soie de verre que l'on détache à l'aide d'une pointe effilée. La baguette, le tube effilé et le bécher sont rincés à l'eau bidistillée.

On titre ensuite en retour jusqu'à coloration rose persistante par le permanganate après avoir ajouté une quantité connue en excès d'une solution d'oxalate de sodium $0.02N$.

La présence de la soie de verre n'est pas gênante car elle se trouve en faible quantité et forme de petites paillettes blanches au fond de la fiole. Il faut prendre la précaution de la laver avant le dosage avec de l'acide sulfurique, puis avec l'eau.

Pour des teneurs comprises entre 0.5 et 1 mg de potassium dans 0.5 ml de solution, les résultats sont approchés à ± 1% en utilisant le matériel microchimique indiqué plus haut.

TABLEAU II

	K. théorique	Trouvé	Erreur relative
En tube de centrifugeuse	0.523 mg	0.518 mg	—1 %
En microbécher	1.047 mg	1.053	+ 0.6%
	,,	1.040	—0.7%
	,,	1.043	—0.4%

Si la mise en solution est faite trop longtemps avant le dosage l'erreur s'abaisse rapidement à —5 pour cent ou davantage. Comme, d'autre part, le virage est difficile à déterminer, cette méthode est très délicate, elle exige beaucoup de soin et elle est beaucoup moins sûre qu'une méthode reposant sur le dosage du cobalt par exemple.

Spectrocolorimétrie

Les essais ont été effectués avec le spectrocolorimètre de JEAN ET CONSTANT. On peut doser les groupements NO_2 ou le cobalt contenu dans le précipité de $[Co(NO_2)_6]K_3.2H_2O$. Dans le premier cas, la méthode par le procédé classique au réactif de Griess a été essayée. Elle ne paraît pas recommandable pour les mêmes raisons que la titrimétrie des groupements NO_2. En effet il est difficile de garder en solution le nitrite provenant de la décomposition du sel complexe un temps suffisamment long pour préparer une série de dosages. D'autre part, il est difficile de préparer une solution étalon de nitrite de titre exactement connu. Toutes ces causes d'erreur rendent le dosage peu sûr. Les meilleurs essais pour des teneurs de potassium de 1 mg donnent des écarts de —2%. Ceux qui sont effectués en microtubes de centrifugeuse, ont toujours fourni des résultats trop faibles par suite d'une dissolution incomplète du précipité dans la soude.

Par contre, la colorimétrie du *cobalt* contenu dans le précipité fournit de bien meilleurs résultats. Ce métal a été dosé grâce à la coloration rouge donnée avec le sel nitroso-R dans une solution amenée exactement à pH 5.5; on a soin d'opérer en présence d'un témoin, ce qui évite l'élimination de l'excès de réactif coloré.

Il est nécessaire de souligner le fait que si l'on se réfère à une courbe d'étalonnage tracée à partir d'un sel de cobalt pur, soit SO_4Co, et le sel nitroso-R, les résultats obtenus pour le dosage du potassium sont constamment trop faibles et représentent environ les 2/3 de la valeur attendue. Comme on a pu le vérifier, cette erreur est due à la présence des nitrites non complètement détruits dans la solution chlorhydrique du précipité. En effet, en examinant la coloration donnée par deux prises d'une même fiole, la première immédiatement après la dissolution du précipité et la deuxième deux jours après, la valeur trouvée trop faible dans le premier cas devient exacte à 1% près dans le second.

Il en est de même si l'on traite une autre prise d'essai par l'eau oxygénée ou si l'on détruit les nitrites par une ébullition prolongée avec l'acide chlorhydrique.

Si de plus, on opère la colorimétrie sur la solution chlorhydrique du mélange $CoO + 3NO_3K$ formé par chauffage à 400° du cobaltinitrite à doser les résultats sont approchés à ± 0.6% près pour des teneurs en potassium de 0.6 mg par ml.

La colorimétrie du cobalt avec le sel nitroso-R s'effectue pour des concentrations en cobalt comprises entre 0.5 γ et 2 γ par ml ce qui correspond à des concentrations en potassium de 1 γ à 4 γ par ml.

TABLEAU III

Quantité de potassium après dilution Théorique	 Trouvée	 Erreur relative
1.97 γ/ml	1.96 γ/ml	—1 %
2.27 γ/ml	2.26 γ/ml	—0.5%
1.48 γ/ml	1.50 γ/ml	+1.3%

Le mode opératoire employé est le suivant: Le précipité contenant par exemple 0.6 mg K/ml est formé soit en microtube, soit en microbécher et lavé comme il est dit plus haut. On le dissout dans quelques gouttes d'acide chlorhydrique *N*/10 et la liqueur est amenée dans une fiole jaugée. On ajoute une goutte de phénolphtaléine (0.1% dans l'alcool) puis quelques gouttes de potasse à 10% jusqu'au virage. On revient ensuite avec quelques gouttes d'acide chlorhydrique *N*/25 et on ajoute encore dix gouttes de cet acide à partir du virage. On a alors amené la liqueur au pH convenable.

Si ces précautions ne sont pas observées les résultats sont faussés quand le pH varie. On ajuste au trait et on prélève une partie aliquote de cette liqueur à laquelle on ajoute ensuite 2 ml d'une solution à 50% d'acétate de sodium (pH entre 5.5 et 6) et 2 ml d'une solution aqueuse à 0.2% de sel nitroso-R et ajuste avec de l'eau bidistillée.

Le tracé de la courbe d'absorption entre 460 et 550 mμ à l'aide du spectrocolorimètre montre immédiatement qu'à 540 mμ l'absorption du témoin est extrêmement faible et d'autre part la région 520-540 mμ est celle de la meilleure sensibilité.

On trace ensuite une courbe d'étalonnage pour des teneurs comprises entre 0.5 γ et 2 γ de Co/ml correspondant à des teneurs en potassium de 1 γ à 4 γ de K/ml. La coloration suit la loi de BEER et est très stable. Le sel utilisé est le sulfate de cobalt anhydre obtenu à 450° par séchage du sulfate cristallisé. La solution étalon a été ensuite dosée microgravimétriquement par la méthode à l'anthranilate de cobalt.

On a effectué des dosages sur des prises d'essai de: 0.18, 0.25, 0.289, 0.579 et 7.12 milligrammes de potassium. En effectuant les dilutions convenables on se ramène à des teneurs de 1 à 2.5 γ de potassium par millilitre. Pour des prises d'essai inférieures à 0.25 mg de potassium l'erreur atteint 2 pour cent.

En conclusion les méthodes colorimétriques basées sur le dosage du cobalt contenu dans le précipité sont plus précises et plus sûres que celles qui sont basées sur le dosage des nitrites. Il faut détruire préalablement les nitrites restant lors de la dissolution du précipité, soit par ébullition, soit par l'eau oxygénée.

Remarque. En se basant sur les remarques faites précédemment sur la présence gênante des nitrites dans la solution, on peut opérer en traçant une courbe d'étalonnage, non pas à partir de solutions de cobalt pur, mais de solutions étalon de potassium traitées par le cobaltinitrite de lithium. C'est ainsi qu'a opéré Madame M. DOAN[1] dans son Diplôme d'Etudes Supérieures pour le dosage du césium par le cobaltinitrite de sodium.

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[1] Madame M. DOAN, *Contribution au dosage colorimétrique du césium*, Diplôme d'Etudes Supérieures, Paris 1952.

Le Tableau IV donne quelques résultats obtenus avec 0.579 mg de potassium.

TABLEAU IV

Quantité théorique	Trouvée en mg	Erreur relative
0.579 mg	0.585	+ 1%
	0.575	— 0.7%
	0.600	+ 3%
	0.582	+ 1%
	0.615	+10%

Comme on le voit, si une partie des nitrites présents est détruite les résultats deviennent trop élevés et la méthode est beaucoup moins sûre.

RÉSUMÉ

Par emploi d'une solution de cobaltinitrite de lithium, l'auteur remarque que le potassium fournit un précipité bien défini $[Co(NO_2)_6]K_3.2H_2O$ lequel peut se prêter aux dosages gravimétrique, volumétrique et colorimétrique de l'ion K^+.

SUMMARY

With a solution of lithium cobaltinitrite, potassium forms a well-defined precipitate of $K_3[Co(NO_2)_6].2H_2O$, which can be used for gravimetric, volumetric and colorimetric determinations of the K^+-ion.

ZUSAMMENFASSUNG

Bei der Verwendung von einer Lithiumkobaltinitritlösung beobachtete die Autorin, dass Kalium einen wohldefinierten Niederschlag $K_3[Co(NO_2)_6].2H_2O$ liefert, der sich zur gravimetrischen, massanalytischen und kolorimetrischen Bestimmung des Kaliumions eignen kann.

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THE IODOMETRIC DETERMINATION OF MANNOSE AND OTHER ALDOSES

by

J. R. COLLINS

Courtaulds Limited, Research Laboratory, Maidenhead, Berks. (England)

INTRODUCTION

Aldoses are quantitatively oxidised to aldonic acids by hypoiodous acid[1],

$$R.CHO + HIO \rightarrow R.COOH + H^+ + I^-, \quad \ldots\ldots\ldots \quad (1)$$

and this reaction has formed the basis for a number of methods for their estimation[2,3]. The methods using dilute caustic alkali and iodine, such as that of KLINE AND ACREE[4], are more generally favoured as being more rapid and, it is said, more consistent than those in which carbonate buffers are used.

In extending the method of KLINE AND ACREE to the determination of mannose, we have found that this sugar can be grossly underestimated. These authors recommend that 1.5 ml to 3.0 ml excess of $N/10$ iodine solution should remain for back-titration at the end of the oxidation, but it has been found that this amount remains even if considerably less than the equivalent amount of iodine is added to a mannose solution. That mannose is oxidised more slowly than many other aldoses was recognized by BOUGAULT[5] who found that whereas a 30 minute reaction time was sufficient for glucose in his method, 90 minutes was required for mannose. Other workers have found that mannose oxidises at approximately one quarter of the rate found for glucose[1].

A method has therefore been evolved for the estimation of the aldose content of a mixture of sugars of which mannose is a constituent. This is but a variation of the older methods using a carbonate solution though with rather more precise conditions under which criticisms concerning the inconsistency of results do not apply.

The conditions influencing reaction (1) may be summarized as alkalinity, iodine and iodide concentration, time and temperature. The reaction is accompanied by a secondary oxidation of both aldoses and ketoses, probably at the primary alcohol group, by the interconversion of aldoses and ketoses and by iodate formation. The conditions must therefore be such that the latter reactions are suppressed as far as possible, while reaction (1) is carried to completion.

The secondary oxidation of aldoses and ketoses appears to be influenced to the same degree by the conditions affecting reaction (1), and the two oxidations are difficult to separate unless the time factor is favourable. Thus in the case of a mixture of glucose and fructose, the primary oxidation of the glucose may be completed before the secondary oxidations of the two sugars has proceeded to an appreciable extent. Conversely, complete oxidation of mannose necessarily involves some secondary oxidation of other sugars present and a successful method of determination must keep the secondary effect at a constant figure. This implies close control of all the conditions mentioned above.

It is particularly desirable to keep the pH of the reaction mixture constant since this will affect the rate of interconversion of aldoses and ketoses. This control of the pH is difficult to achieve using sodium hydroxide solution and a sodium carbonate solution was therefore used as the alkaline medium in the experiments to be described. The rate of interconversion in this solution was not above 0.1% per hour at 20° C (the result of observations to be published elsewhere).

Iodine is partially hydrolysed by water to form hypoiodous and hydriodic acids. The hydrolysis is thus favoured by the presence of alkali and in this case the overall equilibrium may be represented by:

$$I_2 + 2OH^- \rightleftharpoons IO^- + I^- + H_2O, \qquad (2)$$

$$IO^- + H_2O \rightleftharpoons HIO + OH^-. \qquad (3)$$

Since the ratio of the concentration of hypoiodite ions to that of the free hypoiodous acid is fixed by the pH, the two species will be generally referred to as hypoiodite though the free acid appears to be the oxidising agent. The hypoiodite will react further to form iodate irreversibly,

$$3HIO \rightarrow HIO_3 + 2HI. \qquad (4)$$

In the almost complete absence of hydrogen ions, the iodate is stable and does not contribute to the oxidation of the sugars, but reduces the available hypoiodite. By analogy with chlorate formation, reaction (4) would be expected to have a high activation energy, and it would appear from the experiments given below that it is higher than that of reaction (1). The temperature used should therefore be as low as convenient. Additionally the experiments indicate that reaction (4) is of a higher order with respect to hypoiodite concentration than reaction (1), and it is thus an advantage to keep this concentration at a low value.

EXPERIMENTAL

Materials

Glucose, fructose and mannose were recrystallized from reasonably pure commercial samples. The sodium carbonate was of reagent quality and found free from bicarbonate. Other chemicals were of A.R. quality.

Procedure

Reaction solutions in stoppered flasks were kept in a thermostat out of direct sunlight. After the required reaction time, the solutions were acidified with 6*N* HCl and the excess iodine titrated with *N*/10 sodium thiosulphate using starch indicator.

RESULTS

(i) *Iodate formation*

Experiments on the oxidation of mannose at 35° C showed that the rate of iodate formation was altogether too rapid for completion of the oxidation without the use of inconveniently large quantities of iodine. At 20° C, the difference between the rates was much larger and this was selected as the working temperature. A lower temperature might show an even greater difference but is less convenient for general use.

The hypoiodite concentration was now varied with a fixed quantity of iodine added. Reference to equation (2) shows that an increase in iodide concentration will decrease the amount of hypoiodite present[6]. The procedure was to add 25 ml of *N*/10 iodine solution to 25 ml of *N*-Na_2CO_3 solution containing $\frac{1}{80}$ mole of mannose (*i.e.* equivalents of iodine and mannose). The iodine solution contained 20 g per litre of KI, and additional KI was added as required before the solution was left for 30 minutes at 20° C. The iodine used is shown in Table I, the iodide concentration being given in grams per litre of iodine solution. Similar results were obtained with times other than 30 min.

TABLE I

$\frac{1}{80}$ MOLE MANNOSE IN 25 ml *N*-Na_2CO_3 + 25 ml *N*/10 IODINE SOLUTION, 30 min AT 20° C

Potassium iodide g per l	*N*/10 iodine used ml
20	16.4
40	19.9
60	20.7
80	20.6
120	20.0

From this table it is seen that the iodine consumption is highest with 60 g per l of KI. It can be inferred that at lower concentrations of KI, the hypoiodite concentration is large, leading to a high rate of iodate formation. At higher concentrations of KI, the rate of iodate formation is much lower, but the rate of sugar oxidation is also lowered by the reduced hypoiodite concentration.

The iodine solutions for the following experiments were therefore made up to contain 60 g of KI per litre.

(ii) *Control of the secondary oxidation*

For examining the effect of changing conditions on the secondary oxidation, it was convenient to use fructose which does not undergo the primary oxidation. It was necessary to see how far the extent of this oxidation was affected by the proportions of alkali and iodine solutions, and the effect of time and temperature. In all the following experiments, $\frac{1}{80}$ mole fructose was used.

First, 30 ml of N-Na_2CO_3 was taken each time, the quantity of $N/10$ iodine solution being varied. The iodine used after 30 min at 20° C is shown in Table II.

TABLE II

$\frac{1}{80}$ MOLE FRUCTOSE IN 30 ml N-Na_2CO_3, 30 min AT 20° C

$N/10$ iodine added ml	$N/10$ iodine used ml
5	0.21
10	0.40
20	0.50
30	0.45
50	0.61

Secondly, equal volumes of N-Na_2CO_3 and $N/10$ iodine were added to the fructose, the reaction time again being 30 min at 20° C. The results are shown in Table III.

TABLE III

$\frac{1}{80}$ MOLE FRUCTOSE, 30 min AT 20° C

Volume of N-Na_2CO_3 and volume of $N/10$ iodine added ml	$N/10$ iodine used ml
5	0.44
10	0.47
20	0.56
30	0.45
50	0.44

This latter experiment shows that the addition of equal volumes of alkali and iodine solutions has the desired effect of keeping the extent of the secondary oxidation at a reasonably constant value.

The effect of time and temperature is shown in Table IV from which it is seen that close control of both these variables is desirable.

TABLE IV

$\frac{1}{80}$ MOLE FRUCTOSE, 30 ml N-Na_2CO_3, 30 ml N/10 IODINE

		N/10 iodine used, ml		
Minutes	Temperature	15° C	20° C	25° C
15		0.15	0.20	0.42
30		0.30	0.45	0.87
60		0.64	0.93	1.61

(iii) *The excess of iodine required and time of reaction*

The sensibly complete oxidation of mannose to mannonic acid requires either a very large excess of hypoiodite reacting for a short time, or a smaller excess reacting for a comparatively long time. In the first case the large volumes of iodine needed lead to inaccuracy in measurement and in the latter, the secondary oxidation of other sugars present reaches large proportions.

With a reaction time of 15 min at 20° C, it was apparent that three or four equivalents of iodine would be necessary and this was considered to be excessive.

The reaction time was extended to 30 and 60 minutes and the dependence of the iodine consumption upon the iodine added is shown in Table V.

TABLE V

$\frac{1}{80}$ MOLE MANNOSE, EQUAL VOLUMES OF N-Na_2CO_3 AND N/10 IODINE SOLUTIONS, 20° C. THEORETICAL IODINE CONSUMPTION, 25 ml

N/10 iodine added ml	N/10 iodine used, ml 30 min	60 min
35	22.87	24.06
40	23.65	24.58
45	24.13	24.82
50	24.61	24.97
55	24.76	25.08

It was considered that the advantages of the more complete oxidation of mannose at 60 min were nullified by the high secondary oxidation figure of 0.93 ml for fructose (see Table IV). The recommended method is therefore for a 30 ml ± 2 ml excess of iodine (55 ml added) reacting for a time of 30 min. Within these limits of excess iodine, variation of the iodine used by mannose should be within experimental error.

(iv) *Determination of mixtures of sugars*

A number of mannose-fructose and glucose-fructose mixtures were treated with a 30 ml ± 2 ml excess of N/10 iodine for 30 min at 20° C with an equal

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volume of N Na_2CO_3. The amount of iodine used, t, was found to be a linear function of the percentage of aldose, p.

For $\frac{1}{80}$ mole mannose-fructose mixture,

$$t = 0.45 + 0.2445\,p, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

and for $\frac{1}{80}$ mole glucose-fructose mixture,

$$t = 0.45 + 0.2490\,p. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The calculated and observed titrations are shown in Table VI, and the difference between the two would appear to be within experimental error.

TABLE VI

$\frac{1}{80}$ MOLE MANNOSE-FRUCTOSE MIXTURE			$\frac{1}{80}$ MOLE GLUCOSE-FRUCTOSE MIXTURE		
p	$t_{obs.}$ ml	$t_{calc.}$ ml	p	$t_{obs.}$ ml	$t_{calc.}$ ml
0.00	0.45	0.45	0.00	0.45	0.45
10.52	3.04	3.02	10.35	3.04	3.03
20.34	5.44	5.42	19.98	5.43	5.43
30.30	7.83	7.86	29.68	7.87	7.84
39.91	10.21	10.21	39.25	10.25	10.22
49.64	12.64	12.59	48.65	12.54	12.56
59.43	14.97	14.98	58.51	14.97	15.02
69.51	17.46	17.45	68.66	17.57	17.55
79.46	19.76	19.88	78.27	19.93	19.94
89.23	22.23	22.27	87.75	22.25	22.30
100.00	24.90	24.90	100.00	25.35	25.35

(v) *Determination of other sugars*

The method as used in (iv), was found successful with L-arabinose, galactose, cellobiose, lactose and maltose. These sugars all had an iodine equivalent similar to that of glucose.

A test was also made with sorbose, $\frac{1}{80}$ mole of which had an iodine equivalent of 0.96 ml compared with 0.45 ml found for fructose.

THE METHOD OF ESTIMATION

The suggested method for aldose estimation, especially in the presence of mannose, is as follows:

To $\frac{1}{80}$ mole sugar (*i.e.* 0.225 g of hexose) add equal volumes of N Na_2CO_3 solution and of $N/10$ iodine solution, the latter containing 60 g KI per litre. The solution is maintained at 20° C for 30 minutes from the first addition of iodine and then acidified with $6N$ hydrochloric acid. The excess iodine is titrated with $N/10$ sodium thiosulphate; the titre should lie between 28 ml and 32 ml. The iodine used, t, is the difference between this value and that of a blank determination without sugar. The percentage of aldose, p, is given

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(a) where the predominant aldose is mannose by

$$t = 0.45 + 0.2445\ p,$$

(b) where glucose is predominant by

$$t = 0.45 + 0.2490\ p.$$

Where a mixture of aldoses is present and the composition approximately known, the above formulae can be interpolated.

It is obvious that the method may be adapted for the estimation of smaller quantities of sugar by the use of proportionately smaller quantities of carbonate and iodine solutions with a corresponding adjustment to the formulae.

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SUMMARY

A method has been evolved for the iodometric estimation of aldoses with particular reference to mannose. Mannose reacts more slowly with hypoiodite than many other aldoses and secondary reactions become appreciable as the oxidation of this sugar is taken to completion. The conditions affecting the secondary reactions have been investigated and the method which is proposed has been designed to keep the extent of these reactions at a small and constant figure.

RÉSUMÉ

Une méthode a été développée en vue du dosage iodométrique des aldoses, du mannose en particulier. Le mannose réagit avec l'hypoiodite plus lentement que beaucoup d'autres aldoses. Il faut tenir compte des réactions secondaires se produisant lors de l'oxydation de ce sucre. Les conditions influençant les réactions secondaires sont étudiées et une méthode est proposée.

ZUSAMMENFASSUNG

Es wurde eine Methode zur jodometrischen Bestimmung von Aldosen mit besonderer Berücksichtigung von Mannose entwickelt. Die Mannose reagiert mit Hypojodit langsamer als viele anderen Aldosen und Nebenreaktionen werden bemerkbar, wenn die Oxydation des Zuckers ihrem Ende zugeht. Die die Nebenreaktionen beeinflussenden Bedingungen wurden untersucht und die Methode wurde mit der Absicht vorgeschlagen, diese Reaktionen auf einem kleinen und konstanten Ausmass zu halten.

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SEPARATION OF MICROGRAM QUANTITIES OF ALUMINUM AND IRON(III)

by

HARRY TEICHER AND LOUIS GORDON

Department of Chemistry, Syracuse University, Syracuse, N. Y. (U.S.A.)

The separation of milligram quantities of iron(III) from aluminum by passage of an acidic thiocyanate solution through the anion exchanger Amberlite IRA-400A has been previously reported[3]. This paper describes a modification of this procedure to be used for microgram quantities of iron and aluminum. This modification has been utilized in the separation of up to 200 micrograms of iron(III) from comparable amounts of aluminum in order to permit the determination of the latter element in caustic liquors and other alkali products by the spectrophotometric method of KENYON AND BEWICK[1].

MATERIALS USED

Standard aluminum solution. Stock solutions were prepared by dissolving weighed amounts of aluminum ammonium sulfate, Eimer and Amend, Tested Purity Reagent, the purity of which was determined gravimetrically. These solutions contained approximately 0.67 milligram of aluminum and 0.01 ml of concentrated hydrochloric acid per milliliter. More dilute acid solutions were prepared daily as required from these stock solutions.

Standard iron solution. Stock solutions were prepared by dissolving ferrous ammonium sulfate, Analytical Grade, in water; bromine water was added to oxidize the iron. These solutions contained 1.12 mg of iron(III) and 0.01 ml of concentrated hydrochloric acid per milliliter. More dilute acid solutions were then prepared from these stock solutions.

Potassium thiocyanate. (approximately 2.5*M*). The solution was prepared by dissolving 243 grams of salt, Mallinckrodt Analytical Grade, and diluting to 1 liter. The solution was standardized with silver nitrate.

Hydrochloric acid (6*N*).

Sodium hydroxide. This solution was 25% by weight.

Anion exchange resin. Amberlite IRA-400A (Eimer and Amend).

Sodium chloride. This solution, 10% w/v, was prepared from Mallinckrodt Reagent Grade material.

Sodium chloride stock solution. This solution was prepared by dissolving 1100 grams of reagent grade sodium chloride in approximately 4 liters of distilled water. Ammonium hydroxide ($1N$) was added dropwise with stirring until the solution was basic to methyl red (used as an external indicator); the solution was then heated to boiling for a few minutes. After standing overnight the solution was filtered through Whatman No. 40 filter paper.

EXPERIMENTAL

Column preparation

TEICHER AND GORDON[3] indicated the desirability of using the chloride form of Amberlite IRA-400A. The resin was mechanically stirred with $6N$ hydrochloric acid for 30 minutes, rinsed with distilled water, stirred with 25% sodium hydroxide, and then rinsed with water. This complete treatment was then repeated. The resin was stirred with 10% sodium chloride solution for five minutes. This treatment was repeated four times and the resin finally rinsed thoroughly with distilled water until free of acid. This treatment removed impurities from the resin which were found to interfere with the colorimetric determination of aluminum.

The column was then assembled and treated with thiocyanate as previously described[3].

Effect of thiocyanate concentration

Solutions were prepared to contain 50 micrograms of iron(III), 67 micrograms of aluminum, 5.5 grams of sodium chloride in 50 ml, and to be either $0.68M$ or $0.46M$ in potassium thiocyanate. The solutions were then adjusted to pH 2.0 and passed through the column at a flow rate of 8 to 10 ml per minute; the column was washed with ten 10 ml portions of $0.01N$ hydrochloric acid. Blanks were determined with iron and aluminum absent. The eluates were analyzed for aluminum[1] and for iron by the *n*-butanol extraction of ferric thiocyanate from sodium chloride solution[2]. The results are summarized in Table I.

Effect of thiocyanate wash solution

The data of Table I indicated that the separation was more favorable when the solution was $0.68M$ in thiocyanate. However, the quantity of iron in the eluate was sufficient to interfere with the aluminum determination. To ascertain if the hydrochloric acid wash solution was removing the iron, a $0.68M$ thiocyanate wash solution adjusted to pH 2.0 was substituted; the results are summarized in Table II.

The use of the thiocyanate wash solution resulted in a more favorable separation from iron and more complete recovery of aluminum when more than 10 washings were used. The error of approximately 1% is within the error of the colorimetric

TABLE I

EFFECT OF THIOCYANATE CONCENTRATION UPON THE REMOVAL OF IRON(III)

Aluminum recovered*		Iron found in eluate**	
0.46*M* KCNS micrograms	0.68*M* KCNS micrograms	0.46*M* KCNS micrograms	0.68*M* KCNS micrograms
76	63	26	13
75	64	24	14
—	65	—	17
—	67	—	18
—	72	—	21
—	72	—	20
—	71	—	18
—	71	—	18

* 67 micrograms of aluminum taken.
** 50 micrograms of iron(III) taken.

TABLE II

EFFECT OF THIOCYANATE WASH SOLUTION ON RECOVERY OF ALUMINUM

Iron taken micrograms	Iron found micrograms	Aluminum taken micrograms	Aluminum recovered (%) 10 washings	15 washings
50	3.2	67	95	—
50	0.8	67	95	—
50	0.0	67	98	—
50	0.8	67	98	—
101	—	68	—	99
101	—	136	—	99
101	—	272	—	99
100	0.8	67	93	—
100	0.8	67	93	—
100	0.0	67	98	—
100	0.0	67	99	—
200	0.0	67	96	—
200	0.0	67	97	—

determination but it should be noted that the recovery is always somewhat incomplete.

The procedure finally developed was applied to the determination of aluminum in commercial caustic liquors with the exception that 12 washings of the resin column were used instead of the recommended 15. The results are shown in Table III.

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TABLE III

DETERMINATION OF ALUMINUM IN CAUSTIC LIQUORS

Sample	Sample taken for separation grams	Fe_2O_3 found before separation — ppm	Fe_2O_3 found after separation — ppm	Al_2O_3 found after separation ppm
1*	1.50	4.7	1.5	84
	1.52	—	—	94
	1.50	—	0.8	85
	3.77	3.2	0.0	90
	3.75	3.2	0.0	92
	3.76	3.2	—	86
	7.52	3.2	0.0	88
				Average: 89
				Spectrographic: 92
2**	2.87	25.6	3.2	13.3
	2.86	25.6	0.0	13.3
				Average: 13.3
				Spectrographic: 13.2
3**	2.87	—	—	18.1
	2.87	—	—	17.1
	2.87	—	—	16.7
				Average: 17.3
				Spectrographic: 20.4
4*	3.82	7.1	0.6	106
	3.81	6.7	0.7	106
				Average: 106
				Spectrographic: 113
5*	3.80	46.1	0.3	105
	3.81	50.6	0.0	104
				Average: 105
				Spectrographic: 102
6*	3.79	23.0	0.0	6.5
	3.89	23.0	0.0	5.1
				Average: 5.8
				Spectrographic: 3.9
7*	3.78	1.4	0.6	0.0
	3.79	1.0	0.3	0.5
				Average: 0.25
				Spectrographic: 1.2

* 50 weight per cent. NaOH
** 20° Baumé

RECOMMENDED PROCEDURE

Weigh a suitable sample of caustic liquor into a 100 ml beaker and cautiously transfer to a 100 ml Kohlrausch flask containing 70 ml of 6*N* hydrochloric acid, mixing the contents of the flask during the neutralization. Cool and dilute to the proper volume. Transfer 25.00 ml of the solution to a 100 ml beaker, add 4 drops of bromine water, mix well, and allow to stand several minutes. Add 13.5 ml of 2.5*M* potassium thiocyanate and adjust to pH 2.0 with ammonia, using a pH meter standardized at pH 1.0 with a hydrochloric acid-potassium chloride buffer[4]. Transfer the solution to a 50 ml volumetric flask and dilute to the proper volume with 0.01*N* hydrochloric acid.

For a blank, transfer 25 ml of sodium chloride stock solution (5.5 grams) to a 100 ml beaker, add 13.5 ml of 2.5*M* potassium thiocyanate, adjust to pH 2.0 and dilute to the mark with 0.01*N* hydrochloric acid.

Do not allow these solutions to stand more than 3 to 4 hours before continuing the separation.

Place a 250 ml volumetric flask at the outlet of the column and a 125 ml separatory funnel at the top. Pass the blank solution through the column at a flow rate of 8 to 10 ml per minute; do not allow the column to run dry. Prepare a fresh wash solution of 0.68*M* potassium thiocyanate adjusted to pH 2.0 with hydrochloric acid. Wash the column 15 times with 10 ml portions, being certain to rinse the original flask, the separatory funnel, and the walls of the column. Dilute to 250 ml. Analyze suitable aliquots for aluminum[1]; this analysis should be performed within 4 hours of the separation.

The column can be used without regeneration up to the stage where it is almost completely colored by the red ferric thiocyanate complex.

DISCUSSION

The recommended procedure is a modification of the one described in the previous paper[3]. For example, the initial pH and concentration of thiocyanate have been altered. In the original method, some loss of aluminum was noted at pH 2.0 under the prescribed conditions which were designed for macro quantities of the cation. However, there is no apparent loss in the present method up to 200 micrograms of aluminum. Although it would probably be safe to utilize a pH lower than 2.0, *i.e.*, at pH 1.0 as in the previous method, the upper pH limit is recommended here since it avoids a more acidic medium in which thiocyanate is more unstable.

A 0.68*M* ammonium thiocyanate solution was satisfactorily substituted for the 1.5*M* solution used earlier. Fewer washings, fifteen instead of twenty, with a thiocyanate wash solution will result in better than 99% recovery of microgram quantities of aluminum.

The resin required the pretreatment described in the procedure to remove traces of cations which interfered in the subsequent determinations of aluminum[1]. However, this might be an unnecessary step with other analytical methods.

Reagent blanks are determined in an identical manner as with samples being analyzed.

This method for the separation of iron(III) from microgram quantities of aluminum is rapid and accurate. Once a resin column has been prepared, the separation can be effected in about 15 to 20 minutes even by a relatively inexperienced operator. Regeneration of the column can be done with ease. This method was successfully used for about a year in one of the Solvay plants.

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SUMMARY

The separation of microgram quantities of ferric iron and aluminum can be effected by passage of an acidic thiocyanate solution through the anion exchange resin Amberlite IRA-400A. The anionic complex of iron and thiocyanate remains on the column whereas aluminum passes through with the eluate.

This method has been utilized in the separation of up to 200 µg of iron from comparable amounts of aluminum thus permitting the spectrophotometric determination of the latter in caustic liquors and other alkali products.

RÉSUMÉ

La séparation de traces de cations fer(III) et aluminium peut être effectuée par passage d'une solution acide de thiocyanate à travers un échangeur d'anions, la résine Amberlite IRA-400A. Le complexe fer-thiocyanate reste sur la colonne, tandis que l'aluminium passe avec l'éluat. Cette méthode a été utilisée pour la séparation fer-aluminium (jusqu'à 200 µg). Elle permet le dosage spectrophotométrique de l'aluminium dans des liqueurs caustiques et d'autres produits alcalins.

ZUSAMMENFASSUNG

Die Trennung von Milligrammengen von Ferriionen und Aluminium kann durch Durchleiten einer sauren Thiocyanatlösung durch den Harz-Anionenaustauscher Amberlite IRA-400A bewirkt werden. Der Anionenkomplex von Eisen und Thiocyanat verbleibt in der Säule, während Aluminium mit dem Eluat durchläuft.

Die Methode wurde bei der Trennung von bis zu 200 µg Eisen von vergleichbaren Mengen Aluminium verwendet und erlaubte daher die spektrometrische Bestimmung des letzteren in Laugen und anderen Alkalien.

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SEPARATION OF LITHIUM, SODIUM AND POTASSIUM PRESENT AS SULPHATES AND CITRATES BY MEANS OF PAPER CHROMATOGRAPHY

by

D. P. BURMA

Bose Research Institute, Calcutta (India)

The separation by ordinary means of the alkali metals, lithium, sodium and potassium from a mixture is not easy owing to their close physical and chemical properties. The technique of paper chromatography has, however, been of much help in this direction. BURSTALL *et al.*[1] first reported their separation from a mixture of chlorides by means of paper chromatography. Later on CHAKRABARTY AND BURMA[2] as also MILLER AND MAGEE[3] used various solvents in the same technique and separated the alkali chlorides. The separation of alkali hydroxides was effected by BURMA[4] who employed for the purpose both column chromatography on Whatman cellulose ashless powder and paper chromatography. The present communication is concerned with the separation of the three alkali metals in the form of sulphates and citrates.

EXPERIMENTAL

The unidimensional descending technique was followed. The equipment is essentially similar to that of BURSTALL *et al.*[1] with minor modifications. A tall glass cylinder serves as the chamber. Its mouth is kept closed by a cork and made airtight with desiccator grease. 15-20 ml of the solvent kept at the bottom of the cylinder saturates it with the vapour. The cork has two bores, through the one near the border passes the glass rod supporting the chromatographic trough. The central bore is ordinarily kept closed by a small cork. After equilibration of the paper strips within the chamber for about 24 hours, the developing solvent is added to the trough by temporarily opening this central bore. The chromatographic trough consists of a small glass pot fused at the end of the supporting glass rod. Another glass rod bent into the form of a triangle, rectangle, pentagon or hexagon according to necessity and fused to the supporting glass rod just above the pot serves as support for the paper strips. They are held in position in the trough by small glass slides and hang freely over this bent rod. A number of strips can be simultaneously developed depending upon the number of the arms of this bent glass rod. The trough used by BURSTALL *et al.*[1] supported only two strips.

Solvents

Ethanol, methanol and acetone were used for the development. Ethanol of reagent quality was made absolute by repeated refluxing and distillation over quicklime. Methanol and acetone were Baker's analysed samples and were used as such.

Methods of indication

For sulphates. The method of indication of sulphates is based on the fact that a barium salt in a weakly acidic solution gives a red precipitate of barium rhodizonate with a freshly prepared solution of sodium rhodizonate, but solubility of barium rhodizonate is much less than the sulphate, hence on the addition of a sulphate solution to the above, barium is completely precipitated as sulphate and the red colour is either discharged (in weakly acid solution) or changes to yellow (in neutral solution).

The paper strip after development is first uniformly sprayed with $BaCl_2$ solution (100 mg in 50 ml of 70% alcohol), air-dried and then sprayed with the sodium rhodizonate solution (10 mg in 20 ml of 50% alcohol), when the sulphate spots appear as light to deep yellow on a reddish background.

For citrates. The citrates of the alkali metals are made visible on the chromatogram by spraying with bromophenol blue made slightly acid with citric acid. The indicating solution is prepared by dissolving 50 mg of bromophenol blue and 200 mg of citric acid in 100 ml of 70% alcohol. The location of the alkali citrates is shown by intense blue (alkaline) colouration against an orange yellow background.

RESULTS

Table I and Table II record the R_F values of the alkali sulphates and citrates respectively, when applied individually as well as in a mixture and developed with methanol, ethanol and acetone containing various proportions of water. The substances included in brackets in the tables could not be separated under the conditions of experiment.

DISCUSSION

From Tables I and II it is clear that proper adjustment of the composition of the developing solvent leads in most cases to the separation of alkali sulphates and citrates. The important role played by the water-content of the developing solvent as observed by the author[5,6] receives a strong support from these experiments.

In general, the R_F values increase with the increase in water-content of the

TABLE I

R_F VALUES OF ALKALI SULPHATES

	Methanol-water			Ethanol-water				Acetone-water			
Individual	9:1	7:3	5:5	7:3	6:4	5:5	4:6	7:3	6:4	5:5	4:6
Li-Sulphate	.70	.72	.76	.64	.66	.68	.72	.39	.45	.52	.59
Na- ,,	.63	.73	.74	.48	.52	.55	.68	.18	.28	.35	.49
K - ,,	O(dragged)	.63	.72	.18	.31	.43	.64	dragged	.20	.26	.40
Mixture											
Li-Sulphate	.72	single drawn out spot	single drawn out spot	.58	.67	.65 close	single drawn out spot	.38 just septd	.45	.49	.58
Na- ,,	.62			.41	.53	.55			.25 just septd	.36	
K - ,,	O(dragged)			.21	.39	.42		drawn out	.18	.25	.41

TABLE II

R_F VALUES OF ALKALI CITRATES

	Methanol-water					Ethanol-water					Acetone-water				
Individual	9:1	8:2	7:3	6:4	5:5	9:1	8:2	7:3	6:4	5:5	9:1	8:2	7:3	6:4	5:5
Li-citrate	.60	.62	.70	.71	.74	.51	.60	.65	.65	.68	.55	.59	.65	.68	.70
Na- ,,	.50	.54	.57	.61	.63	.18	.30	.43	.47	.52	.29	.45	.54	.54	.64
K - ,,	.30	.33	.42	.49	.52	.15	.28	.33	.33	.46	.24	.33	.47	.50	.58
Mixture															
Li-citrate	.62	.69	.70	.71	.73	.50	.55	.59	.63	.65	.54	.55	.62	.65	.67
Na- ,,	.51	.54	.56	.60	.64	.16	.26	.41	.45	.54	.30	.39	.50	.54	
K - ,,	.30	.33	.41	.45				.29	.31	.47					

developing solvent. In the case of both, the sulphates and citrates lithium salts are found to form the fastest moving spots while potassium salts the slowest. This is in agreement with the observation made in case of alkali chlorides[2]. This implies that the partition coefficient of lithium salts between the two phases formed on cellulose[7] is the lowest of the three alkali metals, or, in other words, the solubility of the lithium salts in the mobile phase is the highest. Unfortunately, however, due to lack of knowledge of the actual composition of the phases formed on cellulose and miscibility of the phases under ordinary conditions it is not possible to determine their partition coefficients. Solubilities of the three sulphates in water are known to be in the order Na > Li > K and in the case of citrates in the order K > Na > Li.

There is, in general, an optimum proportion of the liquid with the developing mixtures which ensure separation of the alkali metals. These proportions depend on the nature of the associated anion. For example, 9:1 methanol: water ratio and no others is effective in separating Li, Na and K present as sulphates, the suitable ratio for citrates may be as low as 3:2. It may be noted here that alkali metals from their chlorides were separated in absolute methanol[1,2].

Similarly in the case of ethanol-water, the optimum water-content varies between 30% and 50% in effecting separation of the alkali sulphates. In case of citrates, as well, water-content of 30-50% is effective in the separations. As chlorides, however, the same metals could be separated by using a smaller water-content, 10-30%[2].

Acetone appears to be less promising in this respect compared to the alcohols. In the case of sulphates a 1:1 or at most 3:2 ratio of the acetone: water mixture was found to be the best, whereas the citrates were almost inseparable with any composition of acetone and water. A 4:1 ratio only was able to separate the three metals in the form of chlorides[2].

The results suggest that the hydroxylic nature of the non-aqueous liquid is of great importance in the choice of the developing solution. The hydroxylic character should neither be strong nor very weak so that it can be easily adjusted by suitably varying the water-content. A prediction of the best solvent mixtures and optimum conditions of separation is only possible on the basis of sufficient data obtained by using a large number of solvents, information about the composition of the two phases formed on cellulose and the partition coefficients of the chromatographed substances between the two phases.

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SUMMARY

The technique of paper chromatography has been applied for the separation of the alkali metals present as sulphates and citrates. The sulphates are made

visible on the chromatogram by spraying the paper at first with barium chloride in 70% alcohol and then with Na-rhodizonate solution. The sulphate spots appear as yellow on reddish background by spraying the paper with an alcoholic solution of bromophenol blue made slightly acid with citric acid. There are different optimum proportions of water in its mixture with methanol, ethanol and acetone for the separation of the metals. These optimum proportions depend also on the nature of the salts used. The significance of the nonaqueous component of the mixture used for developing is briefly discussed.

RÉSUMÉ

La technique de chromatographie sur papier a été appliquée à la séparation des métaux alcalins sous forme de sulfates et de citrates. Les sulfates sont mis en évidence sur le chromatogramme en traitant le papier d'abord par une solution de chlorure de baryum dans l'alcool à 70°, puis par une solution de rhodizonate de sodium. Les taches dues au sulfate apparaissent en jaune sur fond rouge en traitant le papier avec une solution alcoolique de bleu de bromophénol, rendue légèrement acide par l'acide citrique. On utilise différentes proportions d'eau dans ses mélanges avec le méthanol, l'éthanol et l'acétone pour la séparation des métaux. La raison de l'emploi du composé non aqueux du mélange, utilisé pour le développement, est brièvement discutée.

ZUSAMMENFASSUNG

Die Technik der Papierchromatographie wurde zur Abtrennung von als Sulfate und Citrate vorliegenden Alkalimetallen verwendet. Die Sulfate wurden durch das Besprühen des Papiers zuerst mit $BaCl_2$ in 70% Alkohol und dann mit Natriumrhodizonatlösung sichtbar gemacht. Die Sulfatflecken erscheinen beim Besprühen des Papiers mit einer alkoholischen Lösung von mit Zitronensäure leicht sauer gemachten Bromphenolblau gelb auf rötlichen Hintergrund. Es bestehen verschiedene optimale Verhältnisse von Wasser in Mischung mit Methanol, Äthanol und Aceton für die Abtrennung der Metalle. Diese optimalen Verhältnisse hängen ebenfalls von der Natur des benützten Salzes ab. Die Bedeutung der nicht wässrigen Komponente der zur Entwicklung benützten Mischung wird kurz besprochen.

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ELECTROCHROMATOGRAPHY ON PAPER

by

D. P. BURMA

Bose Research Institute, Calcutta (India)

The term electrochromatography is generally applied to denote 'electrophoresis' or 'ionophoresis' on filter paper due to its apparent relationship to 'paper chromatography'. In a rigorous sense, the term should signify those processes in which 'electrophoresis' and 'chromatography' operate simultaneously.

In 1939 STRAIN[1] first utilised electromigration, without flow of solvent, on a column of moist porous adsorbent. The technique of paper ionophoresis was introduced in 1948[2] and since then it has been applied in the solution of numerous problems. Excellent reviews have appeared from time to time[3,4,5]. SVENSSON AND BRATTSEN[6] in 1949 and later on STRAIN AND SULLIVAN[7] utilised electrical migration plus simultaneous flow of solvent for the continuous separation of the solutes. These methods have been studied, modified and extended in scope and applicability[8,9,10,11].

In 1948 HAUGAARD AND KRONER[12] employed a similar procedure and obtained a discontinuous separation of ionised substances. The current was passed at right angles to the direction of flow of solvent on the filter paper. In the present communication, an account is given of the type of electrochromatography mentioned above. The electric field may be applied either in the same direction or at right angles to that of the direction of flow of the developing solvent.

EXPERIMENTAL

In order to make the filter paper sufficiently conducting during the development, it is pretreated with a suitable buffer solution. Whatman No. I filter paper cut into suitable sizes is slowly passed through the buffer solution contained in a photographic tray. The excess solution is allowed to drain off, the wet paper is then carefully placed flat on a smooth glass plate and is squeezed several times by means of a glass roller (made of thick glass rod or of sealed glass tube with lead shots within). The paper is then air-dried. It should be observed that the reproducibility of subsequent measurements depends upon the uniformity of buffer treatment and great care should be taken that this is done properly.

The problem of fixing the electrodes to the paper was solved in the following way. Where the voltage is to be applied at right angles to the flow of solvent, the two edges of the paper (the size of the paper being 40 cm × 20 cm) are painted heavily on both the sides with colloidal graphite (aquadag). The painting is made as uniform as possible and about 2 cm wide. The continuity of this graphite electrode is tested by measuring its resistance after drying. Advantages of such painted electrode are threefold:

(1) no special arrangement is to be made for attachment of electrodes to the paper; this makes the descending way of development easy, since the papers should hang freely and an extra attachment to them is not desirable.

(2) there is no reaction of the developing solvent with the electrode material; and

(3) the applied field is uniform throughout the paper, as the contact between electrode material and the filter paper is intimate.

With voltage applied in the direction of flow of the developing solvent, the end of the paper hanging freely is painted on both sides with colloidal graphite. The stainless steel trough to which the upper end is fixed may be made the other electrode, preferably cathode, otherwise it is likely to be dissolved. In case the top end is to be made the anode, a graphite coating is made just one cm above the starting line of the chromatographed substances.

The electrodes were connected with the help of stainless steel clips to the 220 volt main supply. The current passing through the paper which increased with the distance travelled by the solvent front was recorded by a milliammeter.

In all the experiments reported here, the descending way of development was followed, phenol being invariably the developing solvent. Phenol saturated with water produced water-logging on the buffer-treated paper due to presence of salts, so it was always saturated with the same buffer as was used for the treatment of the paper. Citric acid-phosphate buffers were used. The method of development and indication was as usual.

RESULTS

Eight amino acids of closely lying R_F values have been chosen for the experiments. Of these, two are acidic in nature, two basic and the remaining are neutral. Due to their sparing solubility in water ornithine, cystine, lysine and tyrosine are applied as hydrochlorides.

Table I records the R_F values of the amino acids when they are chromatographed individually at different pH's, (a) in absence of any electric field, (b) when the amino acids start close from the negative electrode and the voltage is applied in the direction of flow of the developing solvent, and (c) when they start close from the positive electrode and the voltage is applied in the direction of flow of the developing solvent.

TABLE I

R_F VALUES OF INDIVIDUAL AMINO ACIDS AT DIFFERENT pH WITHOUT OR WITH VOLTAGE APPLIED IN THE DIRECTION OF FLOW OF SOLVENT

	Without voltage applied				With voltage applied (a) Starting from negative electrode (b) Starting from positive electrode							
					(a)				(b)			
pH	2.2	4	6	8	2.2	4	6	8	2.2	4	6	8
Amino acids												
Aspartic acid	0.20	0.12	0.08	0.06	0.22	0.13	0.11	0.08	0.16	0.08	0.05	0.04
Ornithine	0.13	0.06	0.04	0.10	0.10	0.05	0.05	0.25	0.13	0.09	0.10	0.11
Glutamic acid	0.34	0.21	0.16	0.11	0.32	0.22	0.21	0.15	0.28	0.20	0.13	0.10
Cystine	0.02	0.11	0.05	0.06	0.09	0.10	0.07	0.20	0.06	0.12	0.06	0.05
Lysine	0.19	0.10	0.10	0.19	0.20	0.10	0.08	0.36	0.22	0.13	0.20	0.27
α-Alanine	0.40	0.38	0.32	0.32	0.43	0.37	0.36	0.40	0.41	0.42	0.40	0.34
β-Alanine	0.49	0.39	0.36	0.35	0.46	0.42	0.39	0.42	0.48	0.44	0.42	0.44
Tyrosine	0.54	0.53	0.51	0.52	0.51	0.56	0.56	0.60	0.53	0.57	0.57	0.56

TABLE II

R_F VALUES OF AMINO ACIDS IN STATE OF MIXTURE AT DIFFERENT pH WITHOUT OR WITH VOLTAGE APPLIED IN THE DIRECTION OF FLOW OF SOLVENT

	Without voltage applied				With voltage applied (a) Starting from negative electrode (b) Starting from positive electrode							
					(a)				(b)			
pH	2.2	4	6	8	2.2	4	6	8	2.2	4	6	8
Amino acids (4 *in each group*)												
Aspartic acid	0.22	0.06	0.05	0.05	0.21	0.15	0.12	0.09	0.13	0.08	0.08	0.03
Ornithine	0.13	0.03	0.08	0.10	0.09	0.05	0.03	0.24			0.11	0.08
Glutamic acid	0.33	0.23	0.15		0.31	0.25	0.20	0.13	0.26	0.23		
Cystine*	0.05	—	—	—	0.09	0.11	0.08	0.18	0.03	—	—	—
Lysine	0.18	0.12	0.08	0.19	0.18	0.10	0.09	0.33	0.20	0.13	0.19	0.25
α-Alanine	0.37	0.38	0.31	0.31	0.41	0.38	0.34	0.40	0.43	0.39	0.39	0.36
β-Alanine	0.44	0.43	0.36	0.37	0.47	0.44	0.40		0.54	0.46	0.46	0.42
Tyrosine	0.54	0.57	0.51	0.53	0.65	0.60	0.56	0.60		0.58	0.59	0.55

* always forms elongated spot and merges with others; R_F values recorded are approximate.

Table II records the R_F values of the amino acids under the above three conditions but they are present in suitable mixtures. For instance, aspartic acid, ornithine, glutamic acid and cystine form one mixture and the remaining four another.

References p. 524.

TABLE III

R_F VALUES OF AMINO ACIDS IN STATE OF MIXTURE AT DIFFERENT pH WITH VOLTAGE APPLIED AT RIGHT ANGLES TO THE DIRECTION OF FLOW OF SOLVENT

	pH 2.2		pH 4		pH 6		pH 8	
Amino acids (4 in each group)	R_F	Lateral displacement towards + or —	R_F	Lateral displacement towards + or —	R_F	Lateral displacement towards + or —	R_F	Lateral displacement towards + or —
Cystine	0.06	nil	0.06	0.8 cm + ve	0.03	0.5 cm — ve	0.03	0.3 cm + ve
Ornithine	0.14	1.0 cm — ve	0.07	nil	0.08	nil	0.06	0.6 cm + ve
Aspartic acid	0.25	1.3 cm + ve	0.14	1.0 cm — ve	0.11	1.1 cm + ve	0.09	0.5 cm + ve
Glutamic acid	0.40	1.7 cm + ve	0.28	1.3 cm — ve	0.22	1.5 cm + ve	0.14	1.0 cm + ve
Lysine	0.21	0.2 cm — ve	0.12	0.5 cm + ve	0.09	0.7 cm — ve	0.21	0.8 cm — ve
α-Alanine	0.46	1.1 cm + ve	0.44	0.6 cm — ve	0.40	0.2 cm — ve	0.43	0.3 cm + ve
β-Alanine	0.52	1.0 cm + ve	0.51	1.2 cm — ve			0.49	0.1 cm + ve
Tyrosine	0.62	1.2 cm + ve	0.64	1.4 cm — ve	0.63	nil	0.66	0.7 cm + ve
Leucine	0.88	5.4 cm — ve	0.94	1.0 cm + ve	0.88	3.0 cm + ve	—	—
Isoleucine								
Norleucine								
Phenylalanine								

Table III records the R_F values of the amino acids present in three groups of mixtures, as well as their lateral movements on paper, when the electric field is applied at right angles to the flow of solvent. The four amino acids, *viz.*, leucine, isoleucine, norleucine and phenylalanine introduced in this table as the third group are known to be chromatographically inseparable.

The figures given in these three tables are strictly the R_F values under the influence of the applied field, and are likely to be different from those ordinarily obtained.

DISCUSSION

The data presented in Tables I — III clearly show the effect of electric field on the rate of movement of the amino acids. According to the direction of the field applied the effect may produce better separation or may make the resolution poorer. It should be pointed out that in some cases, even a simple buffer treatment of the paper, but without any applied voltage, makes a better resolution, *e.g.*, α-alanine and β-alanine, which are almost inseparable on untreated paper, form two distinct spots when the paper is pretreated with buffer solution. Similar observations were made by earlier workers[13,14].

The electric field causes, in general, the movement of the acidic amino acids towards the anode and the basic amino acids towards the cathode, as a result of which the resolution is much better. The neutral amino acids are expected to be unaffected by the electric field but this is not so at all pH's. In fact, the direction and rate of movement of an amino acid in an electric field depend upon the pH of the medium in relation to its isoelectric point. For instance, aspartic acid (*cf.* Table III) moves towards the anode at pH 2.2 but at pH 4 it moves towards the cathode and at pH's 6 and 8 again towards the anode. Ornithine moves towards the cathode at pH 2.2, at pH's 4 and 6 there is little or no movement, at pH 8 it moves towards the anode. These observations suggest that for a better resolution the pH of the buffer solution should be adjusted according to the isoelectric point of the amino acid concerned, and the direction of the electric field has to be fixed from a consideration of these two pH's.

This is well illustrated by the behaviour of α-alanine, β-alanine and tyrosine which form two almost coincident spots when developed as usual on untreated paper. With buffer solutions three spots are obtained. If after varying the pH of the buffer solution an electric field is also applied in the direction of the flow of solvent, with the amino acids starting from the negative electrode, the separation is made all the more obvious (Table II, b). Thus, three well-separated distinct spots are formed at pH's 2.2, 4 and 6 but at pH 8 α-alanine and β-alanine again form a single spot.

If the electric field is applied at right angles to the flow of the solvent, the above amino acids along with lysine do not show appreciable improvement so far as their separation is concerned. At pH's 2.2 and 4, four distinct spots are formed no doubt but the spots due to α-alanine, β-alanine and tyrosine lie close to each other. At pH 6, α-alanine and β-alanine do not separate from each other but at pH 8 the resolution is somewhat improved again.

An electric field at right angles to the flow of solvent is almost equivalent to two-dimensional separation in unidimensional development as the Table III shows. The amino acids aspartic acid, glutamic acid, ornithine and cystine are best separated at pH 6.0 in an electric field. At other pH's *viz.*, 2.2, 4 and 8.0 there is separation no doubt but the spots appear dragged on paper.

Attempts to resolve the position isomers, valine, norvaline; leucine, isoleucine, norleucine, etc. from a mixture of them by electrochromatography met with little success. This is perhaps due to their identical or close isoelectric points. As Table III shows, at pH 2.2 leucines along with phenylalanine move towards the cathode whereas at pH's 4 and 6 towards the anode. On alkaline papers spots are distorted.

ACKNOWLEDGEMENTS

Sincerest thanks are due to Dr. D. M. BOSE, Director, Bose Institute for kind interest and to Dr. S. K. MUKHERJEE, Lecturer, University College of Science and Technology, Calcutta for discussion.

SUMMARY

The term 'electrochromatography' is used to denote the specific cases where chromatography and ionophoresis operate simultaneously. The electric field may be applied either in the direction of flow of the solvent or at right angles to it. The filter paper is previously treated with the relevant buffer solution and the developing solvent too is saturated with it. Colloidal graphite painted on the two sides of the paper serves as electrodes.

A detailed study has been made of a number of amino acids at different pH's with phenol-buffer as the developing solvent. On ordinary paper acidic amino acids move towards the anode, basic ones towards the cathode, neutral amino acids do not move at all. Using buffer-treated papers, however, the movement depends upon the pH of the buffer and the isoelectric points of the amino acids. By choice of suitable pH and application of electric field in proper direction amino acids having very close R_F values (except isomers) can be separated from one another.

RÉSUMÉ

Le terme 'électrochromatographie' est utilisé pour désigner la méthode combinée par chromatographie et par ionophorèse. Le champ électrique peut être appliqué soit dans la direction d'écoulement du solvant ou à angle droit. Le papier filtre est préalablement traité avec la solution tampon utilisable, et le solvant, employé pour le développement, est saturé de la solution tampon. Un dépôt de graphite colloïdal sur les 2 côtés du papier sert d'électrodes.

Une étude détaillée a été effectuée sur un certain nombre d'acides aminés à différents pH, avec un tampon au phénol. Sur papier ordinaire, les acides aminés acides migrent vers l'anode et les acides aminés basiques vers la cathode; les acides aminés neutres ne bougent pas. Sur des papiers traités avec une solution tampon, le mouvement dépend du pH du tampon et des points isoélectriques des acides aminés. En choisissant un pH convenable et en appliquant un champ électrique déterminé, les acides aminés ayant des valeurs de R_F très rapprochées (les isomères exceptés) peuvent être séparés les uns des autres.

ZUSAMMENFASSUNG

Der Ausdruck 'Elektrochromatographie' wird zur Bezeichnung der spezifischen Fälle gebraucht, bei denen Chromatographie und Ionenphorese zu gleicher Zeit wirken. Das elektrische Feld kann entweder in Richtung des Stromes des Lösungsmittel oder im rechten Winkel dazu angewendet werden. Das Filterpapier wurde vorher mit der passenden Pufferlösung behandelt und das Entwicklerlösungsmittel wurde ebenfalls damit gesättigt. Auf die beiden Seiten des Papiers aufgestrichener kolloidaler Graphit dient als Elektroden.

Es wurde eine eingehende Untersuchung einer Reihe von Aminosäuren bei verschiedenen pH's mit Phenolpuffer als Entwicklerlösungsmittel unternommen. Auf gewöhnlichen Papier wandern die sauren Aminosäuren zur Anode, die basischen zur Kathode und die neutralen bewegen sich überhaupt nicht. Bei der Benützung von mit Pufferlösung jedoch, hängt die Bewegung vom pH der Pufferlösung und von den isoelektrischen Punkten der Aminosäuren ab. Durch die Wahl eines geeigneten pH's und der Anwendung des elektrischen Feldes in geeigneter Richtung können die Aminosäuren mit sehr nahe beieinanderliegenden R_F-Werten (mit Ausnahme der Isomeren) von einander getrennt werden.

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DETERMINATION OF IRON, ALUMINIUM AND CHROMIUM BY HETEROMETRIC TITRATION WITH PHTHALATE

by

M. BOBTELSKY AND I. BAR-GADDA

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem (Israel)

INTRODUCTION

The preceding experimental material (see previous report No. I) shows a way in which the results obtained may be used for analytical purposes.

The method presented below for the analysis of tervalent metals has the following advantages. The analysis is carried out by one quick heterometric titration of the solution to be analysed with a 50% alcoholic potassium phthalate solution. No previous separation or special preparation are needed. The amount of the metals (in 10 ml volume) needed for analysis is only a few mg and the accuracy of the determination is within a few hundredth of a mg. When a batch of similar analyses is to be made quickly the advantages of the method presented will be most apparent.

The 50% alcoholic solution analyzed may contain iron(III), aluminium or chromium as chlorides, nitrates or sulphates, either separately or in mixture. In a mixture of iron and chromium or iron and aluminium both metals may be determined by a single titration. The method does not allow us to determine chromium and aluminium *separately*. In a mixture which contains both metals, their sum may be determined instead. The results may be obtained from the values measured directly or better from the curve plotted.

RESULTS

We present here the method, the results expected and accuracy in the different cases.

Iron. By dilution of an alcoholic solution of an iron salt, a 50% alcoholic solution which contains 2-10 mg iron in 10 ml volumes is obtained. A 50% alcoholic potassium phthalate solution (0.1-0.05M) is added dropwise from a microburet. The titrated solution is stirred vigorously. A red filter is used. The course of the titration is as follows: on gradual addition of phthalate a clear solution is obtained at first. At a point of the approximate molar ratio 1[Fe(III)] : 1[Phth] a precipitation begins. The density ($D = \log {}^{I_0}/_{I}$) increases on further addition of potassium phthalate. The first maximum optical density point (= quantitative precipitation) is obtained when the insoluble $Fe(III)_2Phth_3$ is precipitated quantitatively. This point may be determined in the *absence* of aluminium or chromium with an accuracy of 1-3%.

Solutions which contain aluminium or chromium and a large excess of iron behave similarly to pure iron solutions.

Aluminium. Solutions containing 1-10 mg of aluminium in 10 ml 50% alcoholic solution ($\sim 1 \cdot 10^{-2}$ *M*) may be titrated with 50% alcoholic phthalate solution at room temperature without a photometer. Under the same working condition as before, a sudden precipitation occurs exactly at the molar ratio 1[Al] :2[Phth]. Under favourable conditions theoretical values are obtained.

Chromium. The same procedure is applied as in the case of aluminium.

Iron and aluminium. If iron and aluminium are both in concentrations of $\sim 1 \cdot 10^{-2} M$ they may be determined by a single titration, under the following conditions. A red filter should be used. The molar concentration of iron should be equal or less than that of aluminium. At higher concentrations of iron the results of the aluminium determination are indefinite. On the other hand if the solution contains a large excess of aluminium a supersaturated solution may be obtained and no precipitation occurs in the presence of iron. To avoid this, known quantities of 50% alcoholic solutions of iron or aluminum may be added before the titration. The approximate molar ratio should be 1[Fe(III)] :(1-3)[Al]. The concentration of iron in the solution should be about 0.01-0.02 *M*. The course of the heterometric titration is as follows. On the dropwise addition of phthalate a clear solution is obtained at first. At the approximate molar ratio of 1[Fe(III)] :1[Phth] a precipitation begins. The maximum optical density point is reached (in this case) *exactly* at the molar ratio of 1[Fe(III)] :2[Phth] (< 1% error). On further addition of phthalate practically no change in the optical density occurs: the undissociated soluble compound $[Al_2Phth_3]^\circ$ is quantitatively formed in solution. As soon as an excess of potassium phthalate is added the density begins to rise again. The titration proceeds quickly until the point of the quantitative formation of $[Al_2Phth_3]^\circ$. A horizontal line drawn through the points obtained during the formation of $[Al_2Phth_3]^\circ$ gives the second break. From the distance between the two breaks the amount of aluminium may be calculated [= Al_2Phth_3].

Iron, aluminium and chromium. The limitations, procedure and the curve obtained are similar to the above. The distance between the two breaks gives the *sum* of aluminium and chromium as $Me(III)_2Phth_2$.

Aluminium and chromium. The same procedure is used as in the case of aluminium. An abrupt precipitation occurs at the molar ratio 1[Me(III)] :2[Phth].

TABLE I

Experiment	Contents of the analyzed solution			Titrated with	Compounds obtained at		Optical density at		Calculated mg introduced			mg Found			mg Error		
No.	$FeCl_3$	$AlCl_3$	$Cr(NO_3)_3$	K_2Phth in alcohol	1st break	2nd break	1st break	2nd break	Fe	Al	Cr	Fe	Al	Cr	Fe	Al	Cr
1	2ml$M/20$	6ml$M/20$	—	$M/10$	$FePhth_2$	$AlPhth_2$	0.78	0.80	5.585	8.091	—	5.585	8.091	—	0.00	0.00	—
2	1ml$M/20$	3ml$M/20$	—	,,	,,	,,	0.19	0.22	2.792	4.045	—	2.792	3.910	—	0.00	—0.135	—
3	1ml$M/20$	2ml$M/20$	—	,,	,,	,,	0.33	0.37	2.792	2.697	—	2.792	2.697	—	0.00	0.00	—
4	1ml$M/20$	4ml$M/20$	—	,,	,,	,,	0.36	0.42	2.792	5.394	—	2.792	5.290	—	0.00	—0.100	—
5	2ml$M/20$	—	6ml$M/20$	$M/5$	,,	Cr_2Phth_3	0.88	0.50	5.585	—	15.602	5.585	—	15.600	0.00	—	0.00
6	2ml$M/20$	—	2ml$M/20$	$M/10$	,,	,,	0.84	0.72	5.585	—	5.201	5.585	—	5.201	0.00	—	0.00
7	1ml$M/20$	—	2ml$M/20$	,,	,,	,,	0.33	0.24	2.792	—	5.201	2.792	—	5.201	0.00	—	0.00
8	—	3ml$M/20$	—	,,	$AlPhth_2$	—	—	—	—	4.045	—	—	4.112	—	—	+0.067	—
9	—	1ml$M/10$	—	,,	,,	—	—	—	—	2.697	—	—	2.697	—	—	0.00	—
10	—	3ml$M/20$	—	,,	,,	—	—	—	—	4.045	—	—	4.045	—	—	0.00	—
11	3ml$M/20$	—	—	,,	Fe_2Phth_3	—	0.68	—	8.376	—	—	8.562	—	—	+0.186	—	—
12	—	—	4ml$M/40$	,,	$CrPhth_2$	—	0.05	—	—	—	5.201	—	—	5.201	—	—	0.00

Only the *sum* of both metals may be determined. No photometer is needed. Under favourable conditions theoretical values are obtained.

Table I contains the results of some heterometric analyses and the maximum optical density values obtained at the breaks (under our experimental conditions). All the titrations were carried out in 50% alcohol. The experiment numbers 9, 10 and 12 were carried out in 90% alcoholic solution. As the results show theoretical values for iron (as [Fe(III)Phth$_2$]) are obtained almost in all cases where mixtures of iron with an excess of aluminium or chromium are analysed. The separate determinations of aluminium and chromium also gave theoretical values.

SUMMARY

A new "heterometric" method was used for the determination of iron, aluminium and chromium. With one titration two of the metals can be determined separately in mixtures.

RÉSUMÉ

Des dosages de fer, aluminium et chrome ont été effectués à l'aide d'une nouvelle méthode dite „hétérométrique". On peut doser deux métaux dans un mélange en une seule titration.

ZUSAMMENFASSUNG

Die Bestimmung von Eisen, Aluminium und Chrom wurde mit Hilfe einer neuen „heterometrischen" Methode ausgeführt. Im Gemisch können zwei dieser Metalle in einer Titration bestimmt werden.

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5:6-BENZOQUINALDINIC ACID AS A COLORIMETRIC REAGENT

by

ANIL KUMAR MAJUMDAR AND BUDDHADEV SEN

Inorganic Chemistry Laboratories, College of Engineering and Technology, Calcutta (India)

Quinaldinic acid and α-picolinic acid were used by MAJUMDAR AND SEN[1,2] for the colorimetric estimation of iron. Further they utilised α-picolinic acid[3] as a masking agent for the separation of aluminium from iron and chromium under controlled pH conditions.

Recently MAJUMDAR and his co-workers found 5:6-benzoquinaldinic acid to be a suitable reagent for the gravimetric estimation of copper[4,5], cadmium[6,7], zinc, manganese, nickel and cobalt[8], magnesium[9] and mercury[10] and their separations from each other. They observed that this reagent could also be used as a colorimetric reagent for ferrous ion with which it forms a red-coloured inner metallic complex which is highly soluble in alkali cyanide solution with intensification of the colour. Stability and solubility of the ferrous 5:6-benzoquinaldinate has been found to be less than that of ferrous quinaldinate which is again much less than the ferrous α-picolinate. The intense colour reaction with 5:6-benzoquinaldinic acid and ferrous ion in presence of alkali cyanide forms the basis for the colorimetric estimation of ferrous ion. Though the cyanide has no influence on the region of maximum absorption, it increases the optical density and enhances the sensitivity of the method.

The ferrous complex in presence of cyanide obeys BEER's law from 0.4 to 20 p.p.m. with Lumetron and from 5 to 50 p.p.m. with Klett-Summerson and the optimum range with minimum relative error is found to be in the region of 2.4 to 14 p.p.m. Several ions as that of the alkali metals, chloride, bromide, iodide, thiocyanate, sulphate, nitrate and salicylate do not interfere. Alkaline earth metals form precipitates with the reagent but measurements in presence of them may be made from their filtrates.

The ferrous complex is of composition $(C_{14}H_8O_2N)_2Fe.3H_2O$ when dried in air but becomes anhydrous on heating to about 160° C.

EXPERIMENTAL

Apparatus and solutions

For the determination of the region of maximum absorption, verification of BEER's law, determination of per cent. relative error to one per cent. photometric error and for the evaluation of the concentration range for optimum accuracy, Lumetron with a cell capacity 16 ml and thickness 20 mm was used, while other measurements including also that of maximum absorption region and verification of BEER's law were made with a Klett-Summerson photoelectric colorimeter having a tube cell of capacity 15 ml and diam. 12 mm[2].

The reagent 5:6-benzoquinaldinic acid, m.p. 187° C, was obtained following the method suggested by MAJUMDAR AND MALLICK[4] and a solution of the reagent sodium benzoquinaldinate was prepared from 1 g of the acid per 100 ml solution. Other chemicals and their solutions were the same as used previously[2].

Colour reaction

The red coloured solution formed by the ferrous ion with the benzoquinaldinic acid in presence of an alkali cyanide has the maximum absorption at 515 mμ (Lumetron) or 520 mμ (Klett-Summerson) and which remains unaffected with different amounts of iron, reagent, cyanide and reducing agents as hydroxylamine hydrochloride and hydrazine sulphate (*cf.* curves in Figs. 1 and 2). Ferrous 5:6-benzoquinaldinate complex is less soluble than the quinaldinate or the picolinate and is also more easily decomposed by both the ammonium carbonate and sodium acetate, whereas the alkali cyanide dissolves the complex and intensifies the colour of the solution and hence its composition may be suggested as $[Fe(C_{14}H_8O_2N)_2(CN)_2]K_2$ (*cf.* MAJUMDAR AND SEN[1,2]). The maximum colour development takes place very quickly on the addition of the reagents and the system is stable for about an hour after which it begins to fade. Temperature over 35° C also helps in the fading of the colour.

Composition of the complex

The ferrous 5:6-benzoquinaldinate complex was prepared by the addition of a cold solution of sodium 5:6-benzoquinaldinate to a cold solution of MOHR's salt containing hydroxylamine hydrochloride to keep the iron in the bivalent state. A red-violet precipitate of the ferrous complex separated. This was filtered, washed with cold water to free it from excess reagent and finally washed with alcohol and dried. The air dried salt contains 3 moles of water but on drying at 160° C becomes completely anhydrous. The iron content of the hydrated and the anhydrous complex was determined by ignition as oxide. The formulae of the complexes may be suggested as $(C_{14}H_8O_2N)_2Fe.3H_2O$ and $(C_{14}H_8O_2N)_2Fe$ respectively as the respective iron content were found to be 10.11 and 11.4 per cent.

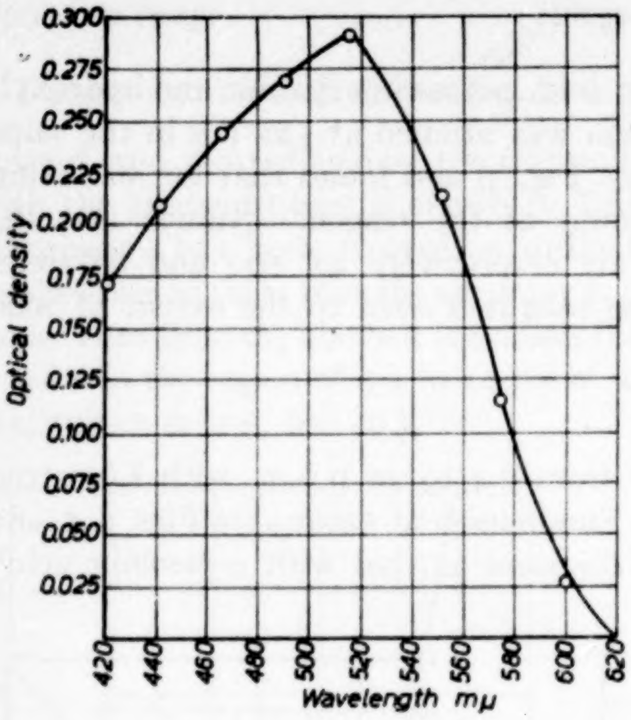

Fig. 1

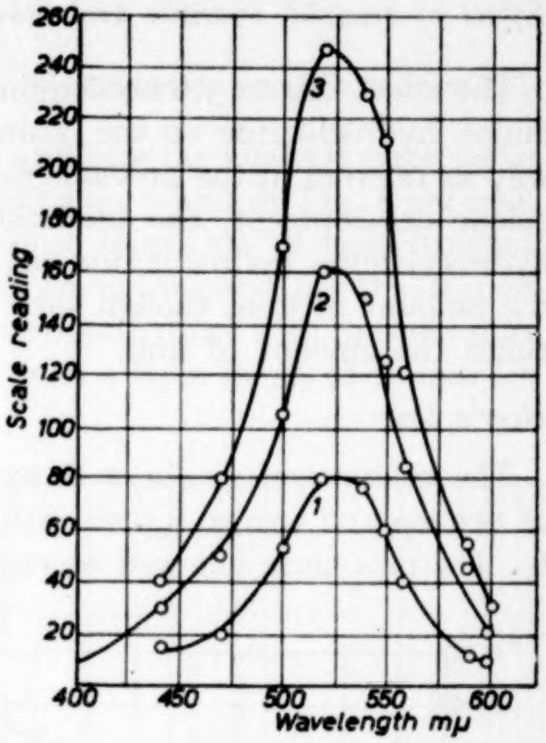

Fig. 2

Fig. 1. Study of the region of maximum absorption of ferrous iron — benzoquinaldinic acid — cyanide system (Lumetron).
Soln.: Iron, $1\cdot10^{-4}$ g; Hydroxylamine hydrochloride, 1 ml; Benzoquinaldinic acid, 1 ml; Potassium cyanide, 1 ml; Total volume, 25 ml.

Fig. 2. Study of the region of maximum absorption of ferrous iron — benzoquinaldinic acid — cyanide system (Klett).
Curve 1. Soln.: Iron, $1\cdot10^{-4}$ g; Hydroxylamine hydrochloride (or 3% Hydrazine sulphate), 1 ml; Benzoquinaldinic acid, 1 ml; Potassium cyanide, 1 ml; Total volume, 20 ml.
Curve 2. Soln.: Iron, $2\cdot10^{-4}$ g; Hydroxylamine hydrochloride, 1 ml; Benzoquinaldinic acid, 1 ml; Potassium cyanide, 1 ml; Total volume, 20 ml.
Curve 3. Soln.: Iron, $3\cdot10^{-4}$ g; Hydroxylamine hydrochloride, 1 ml; Benzoquinaldinic acid, 1 ml; Potassium cyanide, 1 ml; Total volume, 20 ml.

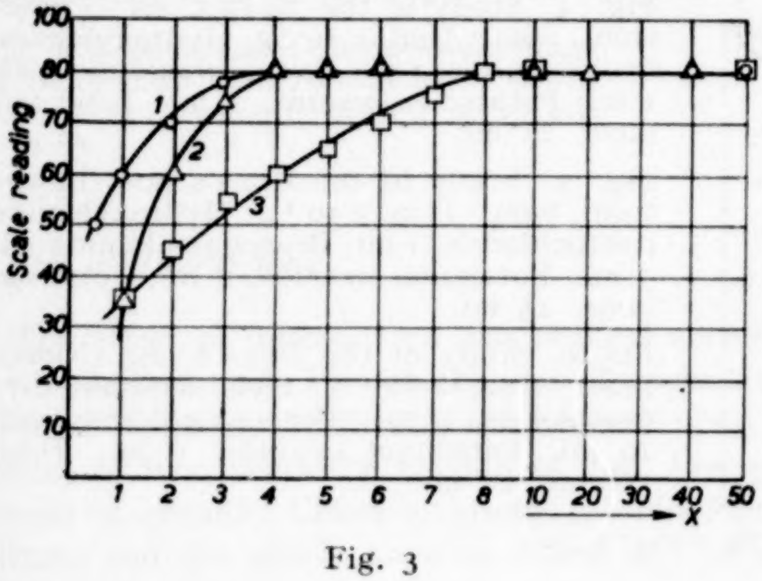

Fig. 3

Fig. 3. Study of the effect of reagents (Klett).
Curve 1. Soln.: Iron, $1\cdot10^{-4}$ g; Hydroxylamine hydrochloride (reducing agent), $x\cdot10^{-3}$ g; Benzoquinaldinic acid, 1 ml; Potassium cyanide, 1 ml; Total volume, 20 ml.
Curve 2. Soln.: Iron, $1\cdot10^{-4}$ g; Hydroxylamine hydrochloride, $4\cdot10^{-3}$ g; Benzoquinaldinic acid, $x\cdot10^{-3}$ g; Potassium cyanide, 1 ml; Total volume, 20 ml.
Curve 3. Soln.: Iron, $1\cdot10^{-4}$ g; Hydroxylamine hydrochloride, $4\cdot10^{-3}$ g; Benzoquinaldinic acid, $4\cdot10^{-3}$ g; Potassium cyanide, $x\cdot10^{-2}$ g; Total volume, 20 ml.

Effect of reagent, cyanide and reducing agents

The effect due to 5:6-benzoquinaldinic acid, potassium cyanide and hydroxylamine hydrochloride on the colour system was studied at 520 mμ in the same way as referred in the previous paper[2] (*cf.* Fig. 3) and found that for maximum colour development, the minimum amount of the reagent, cyanide and the hydroxylamine hydrochloride required are respectively 40, 800 and 40 times the amount of iron, though they can be tolerated even to the extent of 1000 times the amount of iron.

Beer's law

The colour system obeys BEER's law from 0.4 to 20 p.p.m. with Lumetron at 515 mμ and 5 to 50 p.p.m. with Klett Summerson at 520 mμ (*cf.* Figs. 4, 5, and 6). The procedure followed was exactly the same as that with α-picolinic acid[2].

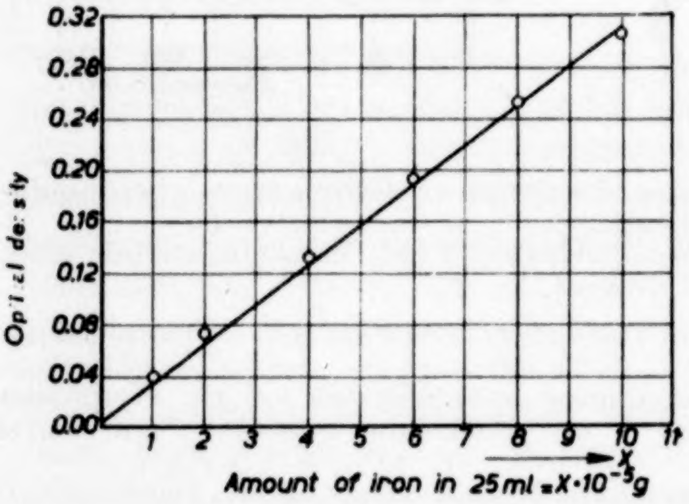

Fig. 4

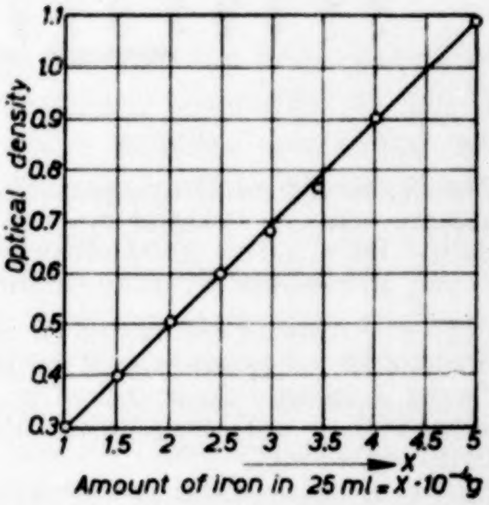

Fig. 5

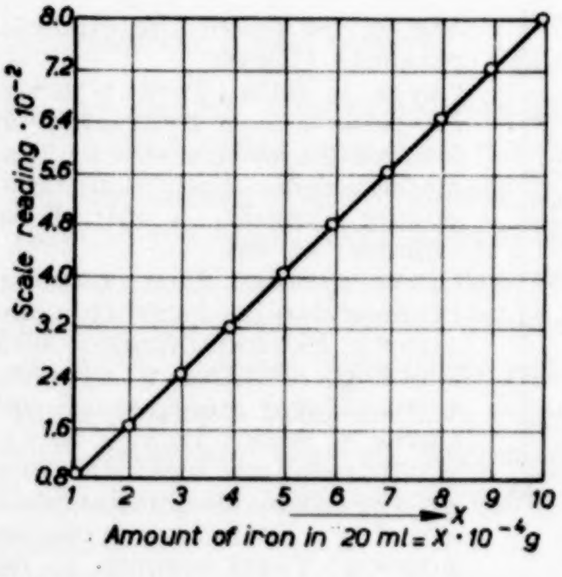

Fig. 6

Fig. 4. Study of the BEER's law (Lumetron). Soln.: Iron, $x \cdot 10^{-5}$ g; Hydroxylamine hydrochloride, 1 ml; Benzoquinaldinic acid, 1 ml; Potassium cyanide, 1 ml; Total volume, 25 ml.

Fig. 5. Study of the BEER's law (Lumetron). Soln.: Iron. $x \cdot 10^{-4}$ g; Hydroxylamine hydrochloride, 1 ml; Benzoquinaldinic acid, 5 ml; Potassium cyanide, 1 ml; Total volume, 25 ml.

Fig. 6. Study of the BEER's law (Klett). Soln.: Iron, $x \cdot 10^{-4}$ g; Hydroxylamine hydrochloride, 1 ml; Benzoquinaldinic acid, 10 ml; Potassium cyanide, 1 ml; Total volume, 20 ml.

Optimum range

The per cent. relative error $(\frac{dc}{c} . 100)$ per 1% photometric error has been calculated and plotted against the transmittancy and how the analysis error varies with the transmittancy is shown in Table I and Fig. 7 and in Fig. 8 per cent. absorbancy has been plotted as ordinates against logarithm of concentration as abscissas to show that the accuracy is greatest where the curve has the steepest slope. Thus from the above it is evident that the optimum range with the minimum error is in the region of 2.4 to 14 p.p.m. of iron with a layer depth of 20 mm (*cf.* MAJUMDAR & SEN, *loc. cit.*).

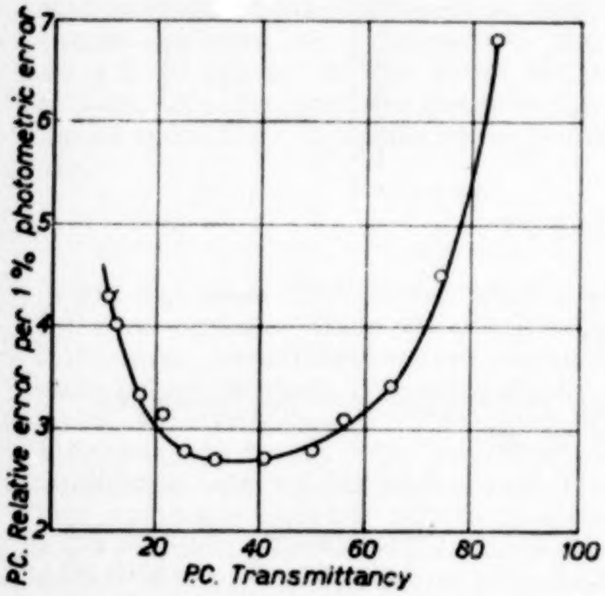

Fig. 7

Fig. 7. Evaluation of per cent. relative error ($dc/c.100$) relative to 1% absolute photometric error (Lumetron).

Fig. 8. Evaluation of the optimum range of BEER's law with 20 mm layer depth (Lumetron). Amount of iron in 25 ml, $x \cdot 10^{-5}$ g.

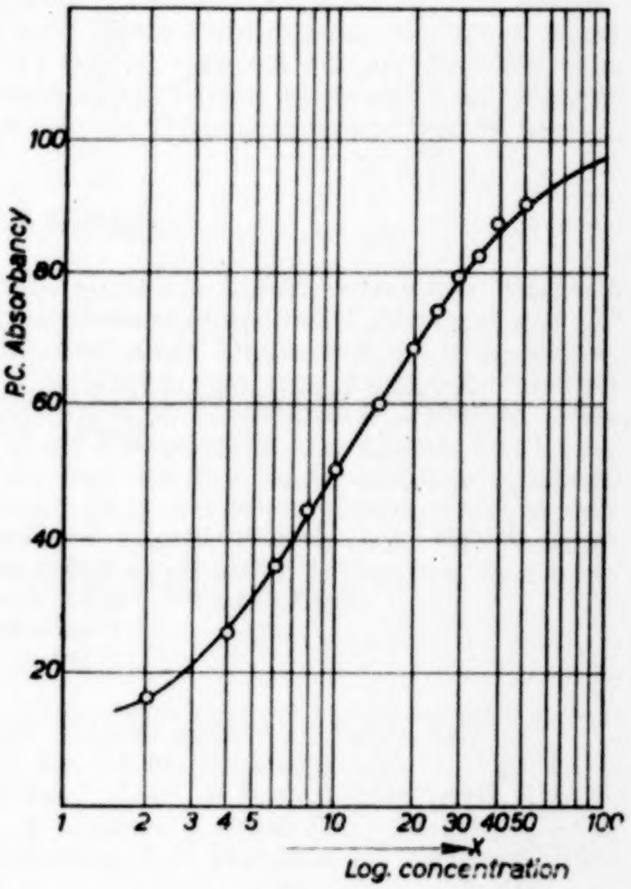

Fig. 8

Effect of diverse ions

The effect of diverse ions was studied according to the procedure followed for α-picolinic acid. Though the ions of magnesium, calcium, barium, strontium form precipitates, the filtrates show normal absorbancy even when present to the extent of 1000 times the amount of iron. Precipitate due to silver dissolves in excess of cyanide. Chloride, bromide, iodide, thiocyanate, salicylate, sulphate, nitrate and the alkalis have no effect (*cf.* Table II).

References p. 535.

TABLE I

MEASUREMENTS WITH LUMETRON. TOTAL VOLUME = 25 ml

Amount of iron $g \cdot 10^{-5}$	% Transmittancy	$\frac{dc}{c}$ .100 (p.c.) relative error per 1% photometric error.
2	84	6.8
4	74	4.5
6	64	3.4
8	56	3.1
10	49.5	2.8
15	40	2.7
20	30.8	2.7
25	25.5	2.8
30	21	3.1
35	17	3.3
40	12.5	4.0
50	10	4.3

TABLE II

MEASUREMENTS WITH KLETT-SUMMERSON PHOTOELECTRIC COLORIMETER
TOTAL VOLUME = 20 ml

Ions	Maximum amount of ion tolerated mg	Ion/Fe ratio at maximum toleration limit	Ions	Maximum amount of ion tolerated mg	Ion/Fe ratio at maximum toleration limit
PO_4^{-3}	0.2	2	Ni^{+2}*	3	30
$CH_3CO_2^-$	2	20	Co^{+2}	0.8	8
$C_2O_4^{-2}$	0.2	2	Th^{+4}**	1	10
Tartrate	0.6	6	UO_2^{+2}	7	70
WO_4^{-2}	0.5	5	Pb^{+2}**	1	10
$Mo_7O_{24}^{-6}$	5	50	Be^{+2}**	0.4	4
HCO_2^-	0.2	2	Al^{+3}***	8	80
F^-	3	30			
$B_4O_7^{-2}$	0.2	2			
Citrate	1	10			
Benzoate	3	30			
VO_3^-	2	20			
Mn^{+2}*	4	40			
Cd^{+2}*	10	100			

* In presence of excess of cyanide

** Measurement with the filtrate

*** Precipitate dissolved in little alkali added after cyanide addition

SUMMARY

5:6-Benzoquinaldinic acid, like α-picolinic acid, has been utilised as a colorimetric reagent for iron (ous). Transmittancy measurements with the Lumetron 402 EF having a cell of capacity 16 ml and thickness 20 mm show that iron from 0.4 to 20 p.p.m. may be estimated, while that with Klett-Summerson photoelectric colorimeter, iron from 5 to 50 p.p.m. may be determined in a tube cell of capacity 15 ml and diam. 12 mm. The optimum range with the minimum error is from 2.4 to 14 p.p.m. The effect of diverse ions, reagent, reducing agent, cyanide and other physical conditions as temperature, time, etc. on the colour system has been investigated.

RÉSUMÉ

L'acide 5:6-benzoquinaldinique, comme l'acide α-picolinique, peut être utilisé comme réactif colorimétrique du fer(II). Avec un appareil Lumetron 402 EF et une cuve de 16 ml, épaisseur 20 mm, il est possible de doser de 0.4 à 20 p.p.m. de fer; tandis qu'avec un colorimètre photoélectrique Klett-Summerson, on peut doser de 5 à 50 p.p.m. de fer. C'est entre 2.4 et 14 p.p.m. que les erreurs sont les plus faibles. D'autre part les auteurs ont étudié également l'effet de divers ions, réactif, agent réducteur, cyanure et les conditions physiques telles que température, temps, etc.

ZUSAMMENFASSUNG

5:6-Benzochinaldinsäure wurde wie α-Picolinsäure als kolorimetrisches Reagenz für zweiwertiges Eisen verwendet. Durchlässigkeitsmessungen mit Lumetron 402 EF mit einem Zellenfassungsvermögen von 16 ml und einer Dicke von 20 mm zeigen, dass Eisen in einer Konzentration von 0.4 – 20 Teilen pro 1000 bestimmt werden kann, während das Klett-Summerson photoelektrische Kolorimeter Eisen in einer Konzentration van 5-50 Teilen pro 1000 in einer Röhrenzelle von einem Fassungsvermögen von 15 ml und einem Durchmesser von 12 mm zu bestimmen erlaubt. Der optimale Bereich mit dem kleinsten Fehler liegt bei einer Konzentration von 2.4-14 Teilen pro 1000. Der Einfluss verschiedener Ionen, Reagenzien, Reduktionsmittel Cyanid und anderen physikalischen Bedingungen wie Temperatur, Zeit usw. auf das Farbsystem wurde untersucht.

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α-PICOLINIC ACID AS A COLORIMETRIC REAGENT
IV. A COMPARATIVE STUDY

by

ANIL KUMAR MAJUMDAR AND BUDDHADEV SEN

Inorganic Chemistry Laboratories, College of Engineering and Technology, Calcutta (India)

The possibilities, scope, accuracy, etc., of the method employing α-picolinic acid as a colorimetric reagent for the estimation of iron have been critically discussed[1]. A study on the effectiveness of the reagent compared to *o*-phenanthroline[2] for the determination of small quantities of iron in naturally occurring samples is the subject matter of the present paper.

EXPERIMENTAL

Apparatus used was the same as used previously and the chemicals used were of high purity.

Solutions of limestones were prepared after decomposition with hydrochloric acid and removal of silica by baking. The quartzite and the sand samples were first hydrofluorised to remove silica and then after fusion with bisulphate were dissolved in dilute sulphuric acid. The solutions were then made up to definite volumes.

Procedure

5 ml of the sample solution were taken in a 20 ml volumetric flask. There the iron was reduced by the addition of an excess of hydroxylamine hydrochloride, about 2 ml, and then were added in succession 2 ml of α-picolinic acid solution and 1 ml of 50 per cent. solution of potassium cyanide. Any precipitate separated during cyanide addition was dissolved by the addition of 1 g NH_4Cl. After dilution to 20 ml to make up the volume, transmittancy of the coloured solution was measured at 440 mμ. Amount of iron was calculated from the mean calibration factor obtained from the transmittancy measurements of a number of known solutions.

Separate 5 ml solutions of the sample were tested with *o*-phenanthroline by the method due to FORTUNE AND MELLON[2] and their transmittancies at 520 mμ were measured. The results were calculated as above (*cf.* Table I).

TABLE I

Sample	Locality	Per cent. Iron by α-picolinic acid	Per cent. Iron by o-phenanthroline
Limestone	Mandla, Jodhpur, Rajasthan	0.099	0.091
Limestone	Haratola, Mundla, M.P.	0.90	0.90
Limestone	Bilaspur, Simla Hill	0.19	0.19
Limestone	Bilaspur, Simla Hill	0.17	0.18
Limestone	Unknown	0.27	0.28
Quartzite	Dhar, Bilaspur, Simla Hill	0.64	0.66
Quartzite	Nihal - Cho	0.067	0.067
Quartzite	Unknown	0.053	0.051
Quartzite	Unknown	0.12	0.13
Quartzite	Unknown	0.033	0.033
Sand	Unknown	0.04	0.04
Sand	Unknown	0.22	0.22

ACKNOWLEDGEMENT

The authors wish to thank the Director, Central Glass & Ceramic Research Institute, Calcutta-32, India, for so kindly providing them with the samples of sand.

SUMMARY

The amount of iron in several naturally occurring samples has been determined colorimetrically with the reagent α-picolinic acid and the results obtained have been found to compare favourably with those due to *o*-phenanthroline.

RÉSUMÉ

Le fer dans différents échantillons naturels a été dosé colorimétriquement au moyen de l'acide α-picolinique et les résultats obtenus peuvent être comparés favorablement à ceux de l'*o*-phénanthroline.

ZUSAMMENFASSUNG

Die in mehreren natürlich vorkommenden Eisenproben vorhandene Eisenmenge wurde kolorimetrisch mit α-Picolinsäure als Reagenz untersucht und es wurde gefunden, dass die erhaltenen Ergebnisse günstig mit den mit *o*-Phenanthrolin erhaltenen verglichen werden können.

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THE SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF IRON AND OF COPPER USING 1,10-PHENANTHROLINE

by

DONALD H. WILKINS* AND G. FREDERICK SMITH

Noyes Chemical Laboratories of the University of Illinois Urbana, Ill. (U.S.A.)

INTRODUCTION

The bis-1,10-phenanthroline complex formed by chelation with Cu(I) was employed by MOSS AND MELLON[1] in the spectrophotometric determination of copper. Such procedure was first suggested through the work of TARTARINI[2]. The same ligand forms a more stable and more intensely colored Fe(II) complex. The ferroin functional group, $=N-\overset{\|}{C}-\overset{\|}{C}-N=$, from 1,10-phenanthroline thus also substitutes as a cuproine functional group, $R-C=N-\overset{\|}{C}-\overset{\|}{C}-N=C-R$ non-selective in the presence of both Fe(II) and Cu(I). Previously the spectrophotometric determination of iron and copper, the one in the presence of the other, necessitated the use of ligands such as terpyridine[3] for the estimation of iron, and 2,2′-diquinoline[4] for the determination of copper, each specific for iron and for copper in the order given. The determination of iron in the presence of copper has been effected otherwise using bathophenanthroline[4].

It is the purpose of the present investigation to describe conditions following which 1,10-phenanthroline may be employed, with specificity, in eliminating the mutual interference of either Fe(II) or Cu(I) when present together, in the simultaneous spectrophotometric determination of trace amounts of these metals. The determinations involving the estimation of the trace contaminants Fe and Cu are of prime importance in the processing of wine, beer, and spiritus liquors to control quality and to prevent storage deterioration. In the preparation and storage, hermetically sealed, of such products as condensed milk, and in the processing and storage of powdered milk or cream and other dairy products, the presence of trace amounts of both iron and copper play an important role in relation to quality control. The established wide distribution and extended application of 1,10-phenanthroline for a multiplicity of analytical procedures[3] serves to enhance the value of the proposed procedure. The application in the use of an immiscible extracting solvent to the isolation of the 1,10-phenanthroline complex formed with Cu(I) is new. An otherwise extremely sensitive color reaction resulting from the formation of the bis-1,10-phenanthroline cuprous complex, is thereby much intensified. At the same time selectivity is provided with respect to the presence of iron.

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GENERAL OUTLINE OF THE PROPOSED PROCEDURE

To the aqueous solution containing copper and iron (total volume 5 ml) is added an excess (1 ml) of a solution of 1,10-phenanthroline in ethanol ($2 \cdot 10^{-5}$ moles per liter). A 2 ml portion of a hydroxylamine hydrochloride free from both iron and copper (0.05 g per ml) is added to form both Fe(II) and Cu(I) chelates. A buffer producing a pH of 8.3 is then added to provide full color development from both chelations. To the solution thus formed, and contained in a 60 ml separatory funnel, there is added 4 ml of *n*-octanol and the reaction mixture shaken two minutes. After 5 minutes standing to provide separation of the two phases the aqueous layer containing the iron complex is withdrawn into a 25 ml volumetric flask and diluted to volume by addition of ethanol. The alcohol layer was then transferred to a 10 ml volumetric flask and likewise diluted to volume by the addition of ethanol. These partitioned solutions of the ferrous and cuprous chelated complex cations are then subjected to spectrophotometric evaluation.

Previous investigations

Moss and Mellon[1] in their study of the colorimetric determination of copper with 1,10-phenanthroline state that "extraction of the color with any of the following solvents is not feasible: *n*-amyl alcohol, benzene, chlorobenzene, chloroform, carbon tetrachloride, ether, and ethyl acetate."

"The 5-chloro, 5-bromo, 5-methyl, 5-nitro, and 5-nitro-6-methyl derivatives of 1,10-phenanthroline have no advantage over the parent compound from the standpoint of sensitivity or stability of the colored complex." 2,2′-bipyridyl is less sensitive and 2,2′,2″-terpyridyl does not react.

Hoste[5] states that among 8 organic ligands (derivatives of pyridine, quinoline and 1,10-phenanthroline) "dipyridyl and *o*-phenanthroline are the only ones not extractable with organic solvents immiscible with water." This limitation applies to the Cu(I) complex cations and includes chloroform as solvent not previously cited as ineffective by Moss and Mellon[1]. Hoste[5] introduced the use of the extraction principle to the spectrophotometric determination of copper employing amyl alcohol as extractant to isolate the Cu(I) complex of 2,2′-diquinoline from aqueous solution. The use of the same organic ligand, but omitting the extraction principle, was originally described by Breckenridge, Lewis and Quick[6]. Hoste[5] gave the trivial name "cuproine" to 2,2′-diquinoline having the copper specific functional group $\mathrm{R\text{-}C{=}N\text{-}\overset{\|}{C}\text{-}\overset{\|}{C}\text{-}N{=}C\text{-}R}$.

Water immiscible organic solvents suitable in the extraction of the copper(I) complex cations formed by reaction with 1,10*-phenanthroline*

The use of *iso*-amyl alcohol, *n*-hexyl and *n*-octyl alcohol as immiscible extraction solvents are herein described as suitable reagents for the quantitative extraction of bis-1,10-phenanthroline cuprous complex cations in their separation from aqueous solution. Other substituted 2,2′-bipyridines[5] and 1,10-phenanthrolines[7,8] having the cuproine functional group are extractable in immiscible solvents when complexed by Cu(I). The introduction of alkyl groups including CH_3 and C_6H_5 for replaceable hydrogen in these ligands enhances this extractability when compared to the parent organic molecule. The same principle is applicable in the case of such alkyl substituted 2,2′,2″-terpyridines when complexed by divalent iron[9]. Lower molecular weight alcohols, for example *iso*-amyl alcohol, serve in the case of these alkyl substituted ferroin and cuproine functional groups containing ligands. In the absence of these alkyl substituents, in the case of 2,2′-dipyridine or 1,10-phenanthroline, as described in the present case, the higher molecular weight alcohols such as *n*-hexyl and *n*-octyl alcohol must be employed as extractants. In such case selectivity is also incorporated in that the copper chelates are extracted and the iron chelates left unextracted in the aqueous phase. From this fact the ferroin functional group serves the same purpose in the separation of the Cu(I) chelate from the Fe(II) chelate as the cuproine functional group effects selectivity in preferential chelation of Cu(I) in the presence of Fe(II). From this principle the more commonly available 1,10-phenanthroline may prove an acceptable substitute for the cuproine reaction ligands, 2,9-dimethyl-1,10-phenanthroline[8] or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline[7] as specifics for copper in the presence of iron.

Qualifications of the new procedure regarding preferential properties

In the opinion of qualified investigators[5] in this particular field of analysis a ferroin, cuproine, or teroine[9] type ligand is profitably promoted only if it meets the following prerequisites.

1. The reagent must be stable, colorless and readily available.
2. It must be specific (singular) or advantageously selective.
3. Its sensitivity should be of a high order in relation to companion reagents which serve the same purpose and may be less commonly available.
4. The color of the chelated metal complex must be stable over an extended period of time under ordinary laboratory working conditions.
5. The chelated complex should preferably be extractable together with the required excess of complexing reagent, through the use of an immiscible solvent. This requirement serves to augment sensitivity and selectivity.
6. The range of pH applicable to the formation of the chelate complexes involved should be broad to liberalize and simplify manipulative procedures.

7. The immiscible solvent should be readily recoverable together with the organic reagent complex for isolation of the ligand employed.

Reagents employed

1. The monohydrate of 1,10-phenanthroline. A solution ($2 \cdot 10^{-5}$ molar) in ethanol.

2. Hydroxylamine hydrochloride. A 5 per cent. aqueous solution free from iron and from copper. Copper if present in reagent grade hydroxylamine is removed by formation of the bathocuproine Cu(I) complex and extraction by use of *n*-hexyl alcohol. The iron, almost always present in reagent grade hydroxylamine hydrochloride, is complexed employing bathophenanthroline and extracted by use of *n*-hexyl alcohol. The hydroxylamine hydrochloride solution is first buffered by the addition of ammonium or sodium acetate to promote complex formation with the phenanthroline. Buffering is not necessary but hastens complex formation.

3. *n*-Octanol. Reagent grade testing free from iron and copper and if necessary purified by re-distillation. Absolute ethanol equally free from Fe and Cu serves for dilutions.

4. Buffer solution pH 8.3. A phosphate buffer is suitable testing free from Fe and Cu.

5. Copper sulfate and ferric sulfate standard solutions. Made from pure iron and pure copper by solution in nitric acid and evaporation to moist dryness with sulfuric acid followed by dilution with water. All sampling operations were on the weight basis.

6. Double distilled water testing to show no iron or copper impurity.

Apparatus employed

1. Separatory funnels. These were stock 60 ml pyrex bulb separatory funnels with the original stopcock removed and 1 mm bore miniature stopcocks substituted to provide a 1 mm bore on the bulb side after attachment to the original bulb reservoir. This gives a minimum diameter meniscus necessary for a sharp separation of aqueous and alcoholic partition volumes of reactants. The separatory funnels were glass stoppered, with standard taper ground closures at both ends. A supporting rack for a dozen such modified separatory funnels is a convenience that it is well to provide.

2. Recording spectrophotometer and accessories. A Cary Model M spectrophotometer and 1 cm quartz windowed observation cells.

3. Weights burets[10] were employed in the preparation of standard copper and iron solutions and for sampling of these solutions in test analyses.

4. A stock of 10 ml and 25 ml volumetric flasks with interchanging glass stoppers and transfer pipets of one and five ml capacity.

Physical constants applied

The molecular extinction coefficient of the 1,10-phenanthroline ferrous complex employed in connection with this work was 11,100[3]. The corresponding molecular extinction coefficient for the same ligand in the form of its Cu(I) complex was given by MOSS AND MELLON as 7030[1], and by HOSTE[5] as 7150. A careful evaluation of the same constant in connection with this work gave 7250. The determination of the optical density was made at 510 mμ for the iron complex and 435 mμ for the copper complex. The relationship Optical Density = Ecl was employed in the calculations where E = molecular extinction coefficient, C = the concentration of metal in gram atoms per liter and l = 1 cm.

Procedure for test determinations

Weighed portions of standard copper and iron solution were transferred to separatory funnels containing 5 ml of water. One ml of the ethanol solution of 1,10-phenanthroline solution was then added followed by 2 ml of the hydroxylamine reducing solution and 5 ml of buffer (pH 8:3).

A 4 ml portion of *n*-octanol was then added and the contents of the separatory funnel shaken for a 2 minute interval. A 5 minute interval was sufficient to permit separation of the two immiscible solvent portions. The top alcohol phase now contains the yellow bis-1,10-phenanthroline Cu(I) complex and the bottom aqueous phase the corresponding tris-ferrous complex.

The aqueous phase was now quantitatively transferred to a 25 ml volumetric flask and diluted to volume using ethanol.

The supernatant *n*-octanol solution was then quantitatively transferred to a 10 ml graduated flask and diluted to volume using ethanol.

EXPERIMENTAL RESULTS

The described procedure was applied to the determination of both iron and copper each in the absence of the other. This established proof of the quantitative partition of each determinant into the proper phase and the ability to separate the two liquid phases quantitatively by a single extraction procedure. The results are given in Table I.

From an examination of the data in Table I, a satisfactorily precise recovery of either copper or iron in a single extraction has been accomplished. Error in the determination of copper or iron was less than 2 per cent. An average of 30% of both estimations were accurate to within less than ± 0.001 milligrams.

The described procedure was applied to the determination of both iron and copper when present together. The results are given in Table II.

From an examination of the data of Table II the error in the determination copper is found to be +2 per cent. and —3 per cent. with 28% of the copper results

TABLE I

THE DETERMINATION OF COPPER AND OF IRON IN A SINGLE PARTITION EXTRACTION. COPPER IN ABSENCE OF IRON AND IRON IN THE ABSENCE OF COPPER

Expt. No.	Copper Added mg	Copper Found mg	Exper. No.	Iron Added mg	Iron Found mg
1	0.049	0.050	7	0.061	0.060
2	0.059	0.060	8	0.075	0.076
3	0.067	0.067	9	0.088	0.088
4	0.078	0.078	10	0.101	0.103
5	0.087	0.086	11	0.113	0.113
6	0.098	0.098	12	0.130	0.131

TABLE II

THE QUANTITATIVE SIMULTANEOUS DETERMINATION OF COPPER AND IRON

Experiment No.	Copper Added mg	Copper Found mg	Iron Added mg	Iron Found mg
1	0.048	0.050	0.064	0.063
2	.057	.059	.077	.078
3	.068	.068	.089	.089
4	.077	.078	.102	.103
5	.086	.086	.115	.116
6	.097	.095	.129	.130
7	.049	.050	.073	.073
8	.059	.059	.079	0.80
9	.068	.067	.078	0.89
10	.076	.074	.077	.079
11	.086	.084	.078	.079
12	.097	.092	.077	.078
13	.050	.050	.129	.130
14	.058	.059	.119	.119
15	.066	.067	.105	.104
16	.075	.075	.088	.088
17	.085	.084	.077	.077
18	0.096	0.094	0.065	0.065

correct to within less than ± 0.001 milligram. The simultaneously determined iron results showed a corresponding positive error of 1.3% and a negative error of 1.1% with 33% of the results correct to less than 0.001 milligram.

Interferences

The new technique herein applied, improves specificity on the part of 1,10-phenanthroline for the determination of copper in that iron is no longer an interference. At the same time the sensitivity of the reagent (molecular extinction coefficient 7250) through the new procedure of extraction from aqueous solution by *n*-octanol is greatly enhanced. 1,10-phenanthroline thus advances from a selective to a specific ligand in Cu(I) determination having a greater sensitivity than 2,2′-diquinoline[5] (cuproine) and equal specificity.

Since the 1,10-phenanthroline-Fe(II) complex remains in the aqueous phase of the two phase partition when the *n*-octanol-water combination is employed in the determination, the same interferences in the determination of iron prevail as those applicable in the chelation of this ligand with Fe(II)[3].

Possible substitution of 2,2′-dipyridine for 1,10-phenanthroline

The complex formed from 2,2′-dipyridine with both Cu(I) and Fe(II) by thorough examination and improvisation does not serve as a substitute for 1,10-phenanthroline. This substitution of the former for the latter ligand (accompanied by decreased sensitivity in the case of both the Cu(I) and Fe(II) complexes formed) was not applicable because of the known diminished stability of these dipyridine complexes when compared with the same complexes employing 1,10-phenanthroline as ligand.

Modification in instrumentation possible

By the procedure as described a selection of optical measuring instruments other than the Cary recording spectrophotometer may be employed, including the General Electric Harding recording spectrophotometer or the Beckman type spectrophotometer. The wavelength frequencies 435 and 510 mμ are requisite only, and any device providing these facilities may be employed in the determination of the optical density as a required evaluation. Filter photometers were not applied in the present investigation but should be applicable even if less sensitive.

SUMMARY

The use of *n*-octanol as extracting solvent has been employed in a new procedure whereby 1,10-phenanthroline provides a simultaneous separation and spectrophotometric determination of both iron and copper when present together. The method depends upon the extraction of the Cu(I) complex into the water-immiscible alcohol phase leaving the Fe(II) complex in the aqueous phase. The separation of the two phase system in one extraction to give a quantitative partition of copper and iron is a feature of the method. The Cu(I) complex with 1,10-phenanthroline was previously thought to be inoperative using any known water-immiscible organic solvent. The corresponding use of 2,2′-dipyridine as a substitute for 1,10-phenanthroline was investigated and found to be inadequate. The new procedure is the first disclosure that the ferroin functional group may serve as a Cu(I) specific in substitution for the cuproine functional group of such ligands as cuproine[5], neo-cuproine[8] and bathocuproine[7]. The new procedure has been demonstrated to give a high degree of precision and at the same time providing simplicity in manipulation.

RÉSUMÉ

Le *n*-octanol, utilisé comme solvant d'extraction, est employé dans un nouveau procédé où la 1,10-phénanthroline permet de séparer et de doser spectrophotométriquement, simultanément le fer et le cuivre; le complexe du cuivre(I) est extrait dans l'alcool non miscible à l'eau, tandis que le complexe du fer(II) reste dans la phase aqueuse. Le fait de pouvoir séparer quantitativement le cuivre et le fer en une seule extraction est une caractéristique de la méthode. Précédemment, on pensait que le complexe du cuivre(I) avec la 1,10-phénanthroline était sans effet, en utilisant les solvants organiques connus non miscibles à l'eau. La 2,2'-dipyridine a été essayée, en vue de remplacer la 1,10-phénanthroline, mais elle n'a pas donné de résultats satisfaisants. Ce nouveau procédé démontra pour la première fois que le groupement fonctionnel ferroïne pouvait être considéré comme un groupement spécifique du cuivre(I), pouvant être substitué au groupement fonctionnel cuproïne de restes tels que la cuproïne[5], la néocuproïne[8] et la bathocuproïne[7]. Ce nouveau procédé permet d'obtenir une grande précision et présente une grande simplicité dans les manipulations.

ZUSAMMENFASSUNG

Die Verwendung von *n*-Oktanol als Lösungsmittel bei Extraktionen wurde in einem neuen Verfahren benutzt, wobei 1,10-Phenanthrolin die gleichzeitige Abtrennung und spektrophotometrische Bestimmung sowohl von gleichzeitig anwesenden Eisen wie Kupfer gestattet. Die Methode beruht auf der Extraktion des Cu-I-Komplexes in die nicht mit Wasser mischbare Alkoholphase und dem Zurückbleiben des Fe-II-Komplexes in der wässrigen Phase. Das Kennzeichen der Methode ist die Trennung des Zweiphasensystems in einer Extraktion, die eine quantitative Verteilung von Kupfer und Eisen ergibt. Früher wurde angenommen, dass der Cu-I-Komplex mit 1,10-Phenanthrolin bei der Benützung irgendeines mit Wasser nichtmischbaren Lösungsmittels nicht extrahiert werden kann. Die entsprechende Verwendung von 2,2'-Dipyridin als Ersatz für 1,10-Phenanthrolin wurde untersucht und als unzureichend gefunden. Das neue Verfahren ist die erste Mitteilung, dass die ferroine funktionelle Gruppe als ein Cu-I-Spezifikum bei der Substitution der cuproinen funktionellen Gruppe von Liganden wie Cuproin[5], Neocuproin[8] und Bathocuproin[7] dienen kann. Es wurde gezeigt, dass das Verfahren mit einem hohen Grad von Genauigkeit arbeitet und zugleicherzeit einfach zu handhaben ist.

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COLORIMETRIC DETERMINATION OF CHROMIUM IN TITANIUM ALLOYS

by
GEORGE NORWITZ AND MAURICE CODELL
Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa. (U.S.A.)

INTRODUCTION

Chromium is an important additive element in titanium alloys, so accurate methods for the determination of chromium in this type of alloy are needed. The methods presently used for the determination of chromium in titanium alloys are volumetric methods. In these methods the chromium is first oxidized to the chromate state with ammonium persulfate in the presence of silver nitrate. The chromium is then titrated potentiometrically with ferrous ammonium sulfate[2,20,45,47], or the solution is treated with an excess of ferrous ammonium sulfate and the excess ferrous ion determined by titration with potassium permanganate[2,20,24,37,46]. Vanadium and tungsten can cause difficulty with the volumetric methods for chromium. Vanadium is titrated together with the chromium when the potentiometric method is used[2,20,45,47]. The presence of vanadium causes difficulty in detecting the end-point in the back-titration method for chromium, because the potassium permanganate slowly oxidizes vanadium from the quadrivalent to the quinquivalent state[2,19,24]. Tungsten can interfere with the potentiometric and back-titration methods for chromium by making the detection of the end-point difficult[2,21]. In the determination of chromium in tungsten steels the tungsten is first precipitated as insoluble tungstic acid by digesting with nitric acid[21,46]. However, with titanium alloys it is not possible to precipitate more than a fraction of the tungsten by such a treatment (or by fuming with sulfuric acid) because of the solvent action of titanium salts on tungstic acid. Volumetric methods are not recommended for the determination of less than 0.05 per cent. chromium in titanium alloys[45].

In view of the shortcomings of the volumetric procedures for the determination of chromium in titanium alloys an investigation was undertaken to develop a colorimetric procedure. Several colorimetric reagents for chromium were considered. The chromate method[7,31] was not satisfactory because it lacked sensitivity and was subject to interference from iron and vanadium. The color of the chromic ion (green) has been used for the colorimetric determination of chromium[10]. However, the method is not sensitive and is subject to interference from many metals. The use of chromotropic salt (disodium – 1, 8-dihydroxy-naphthalene – 3, 6-disulfonate[11,17,35] was not considered satisfactory because titanium, like chromium, gives a red color with the reagent. Chromate will produce a greenish-blue color with aniline hydrochloride[43], but iron, vanadium, etc., interfere. Oxalic acid forms a blue-violet color with chromium that has been used for the colorimetric determination of chromium[44,53]. The method cannot be applied to titanium alloys because of the hydrolysis of the titanium.

The reagent that seemed best for the colorimetric determination of chromium in titanium alloys was diphenylcarbazide. A violet color is obtained with this reagent. To obtain the color the chromium must be in the chromate state. The diphenylcarbazide colorimetric method has been applied to the determination of chromium in tissue[8,48], blood[4,15,48], urine[29,48], fats[40], animal feces[22], leather[18], catgut sutures[52], plant ash[51], sewage[12,41], air[29,38], soils[6,51], milk[50], water[29,51], iron ore[33], rocks[30,51], steels, after removal of the iron by sodium hydroxide[16,25], steels, after removal of the iron by sodium carbonate[1], steels, after removal of the iron by sodium bicarbonate[33], and steels, after complexing the iron with phosphoric acid[23].

In developing a colorimetric procedure for chromium in titanium alloys using diphenylcarbazide various means for oxidizing the chromium to the chromate state were considered. The use of alkaline oxidizing solutions, such as sodium peroxide[3,12], sodium hydroxide and hydrogen peroxide[49], and sodium hydroxide and bromine[13,48] were not satisfactory because the titanium precipitated and occluded some chromium. The use of alkaline fusion mixtures[4,8,40] suffers from the same disadvantage. The use of sodium bismuthate as an oxidizing agent requires conditions that are somewhat critical[48]. Also, the excess bismuthate must be filtered off. The oxidation of chromium by perchloric acid[34,39,50,52] was not considered entirely reliable because of incomplete oxidation of chromium and the danger of loss of chromium by volatilization[14]. The use of potassium permanganate[22,29] was not found to be trustworthy for titanium alloys. The use of ammonium persulfate, together with silver nitrate as a catalyst[2,19,28,33,51], was not found to be reliable for the oxidation of small amounts of chromium in titanium alloys. The best reagent for oxidizing chromium in titanium alloys was found to be a mixture of ammonium persulfate and potassium permanganate in the presence of silver nitrate as a catalyst. For this oxidation a sulfuric acid solution is the only satisfactory medium that can be used. Hydrochloric acid prevents the oxidation. Phosphoric acid causes precipitation of titanium as titanium phosphate. The best acidity for oxidizing the chromium was found to be 25 ml of sulfuric acid per 300 ml. If much less acid than this is used, the titanium will hydrolyze. If much more acid than this is used, the oxidation of the chromium will be incomplete. It was found necessary to oxidize the titanium to the titanic state with hydrogen peroxide prior to the addition of the ammonium persulfate. The silver nitrate catalyst must be added after the ammonium persulfate rather than before. If the silver nitrate is added before the ammonium persulfate, a white precipitate will sometimes appear. This white precipitate was found to be a silver salt, probably the silver salt of some compound of sulfur of lower valence state. After oxidation of the chromium, the permanganate is reduced by boiling with a small amount of hydrochloric acid[2,19,37,46].

The following media have been used for the development of the diphenylcarbazide color: acetic acid[5], hydrochloric acid[5,36,42,52], phosphoric acid[7,23,32], sulfuric acid[1,3,6,7,27,42,48], and mineral acid media containing phthalic anhydride[4,9,29,38]. Since the chromium was oxidized in the proposed method in a sulfuric acid solution, the obvious medium for the color development was sulfuric acid. In any case none of the above media except sulfuric acid would have been satisfactory. The use of an acetic acid medium, or a hydrochloric acid medium, or media containing phthalic anhydride gave strong interference from such metals as molybdenum, iron and vanadium. Phosphoric acid could not be used because of the precipitation of titanium phosphate. In so far as the sulfuric acid medium is concerned the best acidity for the color development has been found to be $0.2N$[23,32]. If the acidity is much less than this, there will be increased interference from molybdenum, iron, vanadium, copper, etc. If the acidity is much greater than this, the color is unstable[23,32].

Previous investigators have pointed out that the chromium diphenylcarbazide color shows maximum absorption at about 540 millimicrons[7,8,23,27]. Iron gives a yellowish-brown color with diphenylcarbazide in a sulfuric acid medium that shows maximum absorption at about 380 millimicrons[4,8,27]. Vanadium gives a yellowish-brown color with diphenylcarbazide in a sulfuric acid medium that starts to fade after a few minutes[32]. In this laboratory it was found that by reading the chromium diphenylcarbazide color at 580 millimicrons after 10 minutes, no interference would be encountered from iron or vanadium in the determination of chromium in titanium alloys. Molybdenum gives a reddish color with diphenylcarbazide in a dilute sulfuric acid medium. However, the color is so exceedingly faint that the interference was negligible for the amounts of molybdenum found in titanium alloys.

Commercial chromium-titanium alloys were found to be readily soluble in dilute sulfuric acid (25 ml of sulfuric acid + 160 ml of water). The complex double carbide $Fe_3C.Cr_4C$ that makes high chromium steels difficultly soluble in dilute sulfuric acid[26] is not found in commercial titanium alloys.

The method proposed in this paper is designed for titanium alloys containing 0.02 to 4 per cent. chromium.

APPARATUS AND REAGENTS

Coleman Universal Spectrophotometer, Model 14, with optically matched $105 \times 13 \times 13$ mm cuvettes and a PC-4 filter were used.

Dilute Hydrogen Peroxide. Dilute 15 ml of hydrogen peroxide (30 per cent.) to 100 ml with water.

Ammonium Persulfate Solution (15 per cent.). Dissolve 37.5 grams of cp ammonium persulfate in water and dilute to 250 ml with water.

Silver Nitrate Solution (1 per cent.). Dissolve 10 grams of cp silver nitrate in water and dilute to 1 liter with water.

Potassium Permanganate Solution (3 per cent.). Dissolve 30 grams of cp potassium permanganate in water and dilute to 1 liter with water.

Hydrochloric Acid (1 to 3). Add 100 ml cp hydrochloric acid (sp. gr. 1.18) to 300 ml of water.

Sulfuric Acid (25 ml per 500 ml). Add 25 ml of sulfuric acid (sp. gr. 1.84) to water and dilute to 500 ml with water.

Diphenylcarbazide Solution (0.25 per cent.). Dissolve 0.125 gram of cp diphenvlcarbazide in 95 per cent. ethyl alcohol and dilute to 50 ml with alcohol. Prepare fresh daily.

Standard Chromium Solution No. 1 (1 ml = 0.010 mg Cr). Dissolve 2.8283 grams of pure $K_2Cr_2O_7$ in water and dilute to 1 liter in a volumetric flask. Pipette 20 ml of this solution into a 2-liter volumetric flask and dilute to the mark with water.

Standard Chromium Solution No. 2 (1 ml = 1.0 mg Cr). Dissolve 2.8283 grams of pure $K_2Cr_2O_7$ in about 300 ml of water. Add 5 ml of sulfuric acid and 3 grams of sodium sulfite (to reduce the chromium to the chromic state). Boil until the sulfur dioxide has been driven off. Cool and dilute to 1 liter in a volumetric flask.

METHOD

Preparation of calibration curve

Measure the following aliquots of Standard Chromium Solution No. 1 into 50 ml volumetric flasks: 0.5 ml, 1 ml, 2 ml, 3 ml, 5 ml, 8 ml and 10 ml. Add 5.0 ml of dilute sulfuric acid (25 ml per 500 ml). Dilute to about 40 ml with water and swirl. Add 2.0 ml of diphenylcarbazide reagent and swirl. Dilute to the 50 ml mark with water and shake. In 10 to 40 minutes compare the color with the reagent blank at 580 millimicrons. Plot the per cent. transmittance against per cent. chromium. One ml of Standard Chromium Solution No. 1 is equivalent to 0.1 per cent. chromium. The calibration curve obtained by the authors is shown in Figure 1.

Procedure

Add 160 ml of water and 25 ml of sulfuric acid to a 1-gram sample contained in a 600 ml beaker. Heat on the hot plate until the sample is dissolved. Remove

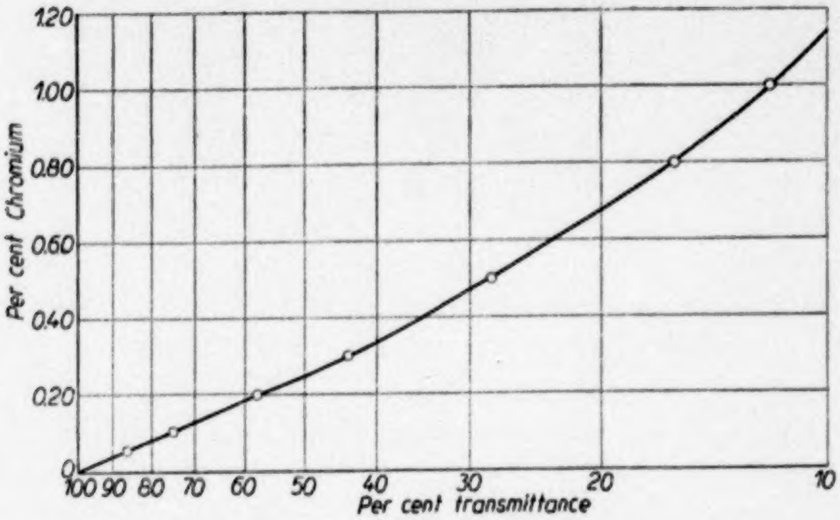

Fig. 1. Calibration curve for the colorimetric determination of chromium in titanium alloys (5 ml aliquot).

from the hot plate and dilute to about 300 ml with water. Add dilute hydrogen peroxide with a medicine dropper until the blue titanous color just about disappears, or until a faint titanium peroxide color appears. Heat to boiling and boil for a minute or two. Remove the beaker from the hot plate. Add in order 20 ml of ammonium persulfate solution (15 per cent.) and 10 ml of silver nitrate solution (1 per cent.). Place the beaker back on the hot plate. Add potassium permanganate solution (3 per cent.) with a medicine dropper until the solution is definitely pink and then add a few drops in excess. Heat to boiling and boil 10 minutes. Be sure that the solution boils and does not just simmer. The boiling is necessary to ensure the destruction of the ammonium persulfate. If the permanganate color should disappear during the boiling, add more potassium permanganate solution. Add 3 ml of hydrochloric acid (1 to 3) and boil 10 more minutes. If the permanganate color does not disappear during the first 2 minutes of boiling, add 2 more ml of hydrochloric acid (1 to 3). Remove the beaker from the hot plate and cool in a running water bath. Transfer to a 500 ml volumetric flask. Dilute to the mark and shake. Allow to stand a half hour or more so that the silver chloride will settle out.

Pipette an aliquot of the solution into a 50 ml volumetric flask. For a sample containing up to 1 per cent. chromium use a 5 ml aliquot; for a sample containing 1 to 2 per cent. chromium use a 2 ml aliquot; for a sample containing 2 to 4 per cent. chromium use a 1 ml aliquot. When measuring out a 1 ml aliquot use a 1 ml pipette graduated in tenths. If a 1 or 2 ml aliquot is used, bring the volume up to 5 ml by the addition of dilute sulfuric acid (25 ml per 500 ml). Dilute the solution to about 40 ml with water and swirl. Add 2.0 ml of diphenylcarbazide reagent and swirl. Dilute to the 50 ml mark and shake. In 10 to 40 minutes compare the color with the reagent blank at 580 millimicrons. The reagent blank is prepared by diluting 5 ml of dilute sulfuric acid (25 ml per 500 ml) to about 40 ml with water, adding the 2.0 ml of diphenylcarbazide reagent and diluting to 50 ml with water. Convert the reading to per cent. chromium by consulting the calibration curve. If a 2 ml aliquot was taken, multiply the result as read from the curve by 2.5. If a 1 ml aliquot was taken, multiply the result as read from the curve by 5.

RESULTS AND INTERFERENCES

The results obtained for chromium in synthetic samples prepared by adding Standard Chromium Solution No. 2 to 1 gram samples of titanium metal are shown in Table I.

TABLE I

RESULTS FOR CHROMIUM IN SYNTHETIC SAMPLES OF TITANIUM ALLOYS

Chromium Present (%)	Average Chromium Found (%)	Standard Deviation (%)	No. of Determinations
0.020	0.022	0.004	5
0.100	0.100	0.007	5
0.500	0.500	0.014	6
1.00	1.01	0.018	5
2.00	1.99	0.044	5
4.00	4.01	0.105	5

TABLE II

RESULTS FOR CHROMIUM IN CHROMIUM-TITANIUM ALLOYS

Sample	Chromium Present (%)*	Chromium Found (%)	Average Chromium Found (%)	Standard Deviation (%)
WA3**	0.15	0.16 0.15 0.15 0.15 0.15	0.152	0.004
WA7***	2.11	2.10 2.10 2.05 2.05 2.00	2.06	0.041
WA12**** (Type Ti-150A)	2.75	2.80 2.85 2.75 2.75 2.70	2.77	0.057

* As determined potentiometrically
** Contains 0.31 C, 0.3 Al
*** Contains 0.07 C, 2.7 Fe, 2.1 Mo, 0.1 W, 0.06 N
**** Contains 0.06 C, 1.3 Fe

TABLE III

RESULTS FOR CHROMIUM IN TITANIUM ALLOYS IN THE PRESENCE OF POSSIBLE INTERFERENCES

Element	Added As	Amount Added (%)	Cr Added (%)	Cr Found (%)
Iron	Metallic Iron	10	0.00	0.00
,,	,,	,,	0.10	0.11
,,	,,	,,	0.50	0.52
Vanadium	V_2O_5	5	0.00	0.00
,,	,,	,,	0.10	0.10
,,	,,	,,	0.50	0.48
Molybdenum	$(NH_4)_6Mo_7O_{24}\ 4H_2O$	10	0.00	0.015
,,	,,	,,	0.10	0.11
,,	,,	,,	0.50	0.49
Tungsten	$Na_2WO_4.2H_2O$	5	0.00	0.00
,,	,,	,,	0.10	0.10
,,	,,	,,	0.50	0.49
Aluminum	$Al_2(SO_4)_3.18H_2O$	5	0.10	0.10
Copper	$CuSO_4.5H_2O$	5	0.10	0.10
Cobalt	$CoSO_4.7H_2O$	5	0.10	0.10
Nickel	$NiSO_4.6H_2O$	5	0.50	0.49
Silicon	$Na_2SiO_3.9H_2O$	5	0.10	0.10
Calcium	$CaSO_4.2H_2O$	5	0.50	0.48
Magnesium	$MgSO_4$	5	0.50	0.51
Tin	Metallic Tin	5	0.50	0.50
Manganese	$MnSO_4.H_2O$	10	0.50	0.49
Boron	H_3BO_3	1	0.10	0.11
Phosphorus	$(NH_4)_2HPO_4$	1	0.50	0.48

The results obtained for chromium in three chromium-titanium alloys are shown in Table II. The results obtained colorimetrically compare well with the results obtained potentiometrically.

The results obtained in the presence of possible interfering elements are shown in Table III. None of the elements found in commercial titanium alloys interferes with the method. In order to oxidize the chromium in the presence of the phosphate it was found that a large excess of silver nitrate solution (25 ml) was necessary, because of the initial precipitation of the silver as silver phosphate. The necessity of adding the excess silver nitrate solution would rarely arise, since commercial titanium ordinarily does not contain more than traces of phosphorus. As can be seen from content of the alloys listed in Table II, neither carbon nor nitrogen interfere with the procedure.

SUMMARY

Chromium-titanium alloys are becoming increasingly important because of their strength and corrosion resistance. Therefore, accurate methods for the determination of chromium in this type of alloy are needed. A colorimetric procedure for the determination of chromium in titanium alloys is proposed. In this method the chromium is oxidized to the chromate state by means of ammonium persulfate and potassium permanganate in the presence of silver nitrate as a catalyst. Diphenylcarbazide is then added to an aliquot of the solution, and the violet color read in 10 to 40 minutes at 580 millimicrons. None of the elements found in commercial titanium alloys, including iron, vanadium, molybdenum, and tungsten, interferes with the method. The proposed method is superior to the volumetric method for the determination of small amounts of chromium. The method is designed for titanium alloys containing 0.02 to 4 per cent. chromium.

RÉSUMÉ

Les alliages chrome-titane deviennent de plus en plus importants, en raison de leur dureté et de leur résistance à la corrosion. C'est pourquoi des méthodes précises pour le dosage du chrome dans ce type d'alliage sont nécessaires. Un dosage colorimétrique du chrome dans les alliages de titane est proposé, le chrome est oxydé à l'état de chromate au moyen de persulfate d'ammonium et de permanganate de potassium en présence de nitrate d'argent comme catalyseur. La diphénylcarbazide est ensuite ajoutée à une partie aliquote de la solution et la coloration violette est mesurée après 10 à 40 minutes à 580 millimicrons. Aucun élément pouvant se trouver dans les alliages de titane commerciaux, y compris le fer, le vanadium, le molybdène et le tungstène, gênent. Cette méthode est plus avantageuse que la méthode volumétrique pour le dosage de faibles teneurs en chrome; elle convient pour des teneurs de 0.02 à 4% de chrome dans les alliages de titane.

ZUSAMMENFASSUNG

Chrom-Titan-Legierungen nehmen wegen ihrer Festigkeit und ihrer Korrosionswiderstandsfähigkeit an Wichtigkeit zu. Es sind deshalb genaue Methoden zur Bestimmung von Chrom in Legierungen dieser Art nötig. Es wird ein kolorimetrisches Verfahren zur Bestimmung von Chrom in Titanlegierungen vorgeschlagen. Bei dieser Methode wird Chrom zum Chromat mit Ammoniumpersulfat und Kaliumpermanganat in Gegenwart von Silbernitrat als Katalysator oxydiert. Dann wird Diphenylcarbazid zu einem aliquoten Teil dieser Lösung hinzugefügt und die violette Farbe in 10-40 Minuten bei 580 μm abgelesen. Keines der in handelsüblichen Titanlegierungen vorhandenen Elemente, einschliesslich Eisen, Vanadium, Molybdän und Wolfram stören bei dieser Methode. Die vorgeschlagene Methode ist der volumetrischen Methode zur Bestimmung kleiner Mengen Chrom überlegen. Die Methode ist für Titanlegierungen mit einem Gehalt von 0.02-4% Chrom bestimmt.

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COLORIMETRIC DETERMINATION OF CARBON IN TITANIUM

by

MAURICE CODELL, GEORGE NORWITZ AND ORIEN W. SIMMONS

Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa. (U.S.A.)

INTRODUCTION

Carbon is often present in titanium metal. Carbon is not an effective hardening agent for titanium, but it is frequently present as an impurity picked up from graphite crucibles or carbon electrodes used to melt the metal. The common method for the determination of carbon in titanium is the combustion method[13]. This method, however, as shown by an inter-laboratory project sponsored by the Department of the Army, leaves something to be desired. A high temperature (at least 2500° F) and an accelerator are required. Furthermore, the sample must be in a fine state of subdivision to prevent some of the metal becoming entrapped by the titanium oxide formed by the combustion. Since titanium is a very refractory material, this entrapment error can be quite serious. In view of the difficulties involved and the inconsistent results obtained in the determination of carbon in titanium by combustion, an investigation was undertaken to develop a colorimetric method for the determination which would depend upon the yellow nitrated organic complex obtained when nitric acid dissolves carbides.

COLORIMETRIC CARBON IN STEELS

The colorimetric determination of carbon was first proposed by EGGERTZ for the determination of carbon in steels[3]. EGGERTZ' method was popular for some time, but gradually lost its importance for the following reasons:

1. Iron itself gives a yellowish coloration to the nitric acid solution that can modify the carbon color in a complex manner[7,14].

2. Many elements present in steels affect the color. Nickel and manganese[6,12,15] and also phosphorus[4] can cause low results. Sulfur can interfere by the formation of a turbidity[2,7]. Chromium, copper, vanadium, cobalt and nickel can cause high results[6,7,10,12,15]. If the method were applied to pure iron, such interferences would be avoided. However, pure iron is not a commercially important product.

Iron and steel as manufactured commercially frequently contain the above interfering elements, especially phosphorus, sulfur and manganese.

3. The form of the carbon in steel has a marked effect on the color obtained[1,5,6,7,10,11,12,14,15]. Carbon can occur in iron and steel as iron carbide (cementite), as a solid solution of iron carbide in iron (martensite, austenite) and in an uncombined state (graphitic carbon). As has been described by HALL AND WILLIAMS[5], iron carbide, when present as such in steels, decomposes into a brown flocculent residue on the addition of nitric acid. The residue goes into solution at about 80° C to form the yellow carbon color. The iron carbide held in solid solution by iron is more soluble in nitric acid than free iron carbide. It is dissolved in nitric acid at room temperature without the formation of the flocculent residue. However, the color is not the same as that produced by an equal percentage of carbon present as free iron carbide. This difference in behavior of the two forms of iron carbide is caused by the colloidal nature of the solid solution of iron carbide in iron. Carbon, when present as graphitic carbon, is not attacked by dilute nitric acid and remains as a black residue in the solution. The manner in which the carbon is present in steels depends upon the amount of carbon present and the heat treatment to which the steel is subjected. For instance, free iron carbide is present in all annealed steels, but if this steel is quenched from its critical temperature, the iron carbide will be retained in solid solution. Also, at a high temperature under certain conditions iron carbide can be broken down into iron and graphite.

4. Steel produced by different processes, for instance by the open hearth process, the Bessemer process, or the crucible process, will give different colors for the same percentage of carbon[1,5,6,7,10,11,12,14,15].

5. Large drillings of steel will give different colors from small drillings[6,12,15].

6. The acid concentration is somewhat critical for the determination of carbon in steels. Insufficient acid will cause a darker tinge[1,11]. Different percentages of carbon require different amounts of acid[1,2,7,11].

7. The heating time required to develop the color varies from 5 to 45 minutes, depending on the amount of carbon present in the steel[7].

8. The coloration obtained when testing steels is unstable[7,10,11].

COLORIMETRIC CARBON IN TITANIUM

The colorimetric determination of carbon in titanium metal (using a nitric-fluoboric-sulfuric acid medium or a nitric-hydrofluoric acid medium) does not have the above disadvantages for the following reasons:

1. Titanium in the titanic state (oxidized with nitric acid) is colorless.

2. "Commercially pure" titanium contains insignificant amounts of nickel, manganese, phosphorus, sulfur, chromium, copper, vanadium, cobalt and other

elements that might interfere with the determination. "Commercially pure" titanium metal is an important industrial item, because it has excellent physical properties and is as corrosion resistant as titanium alloys.

3. The phase relationships of the titanium-carbon system are much different from the phase relationships of the iron-carbon system. For instance, free carbon (graphite) is not encountered in titanium. The subtleties of the carbon coloration observed with steels have not been observed with titanium. A yellow flocculent residue was never obtained on the addition of nitric acid. Heat treatment does not appreciably affect the manner of combination of carbon in titanium.

4. Titanium metal produced by different processes will give the same color for carbon.

5. Large drillings and small drillings will give the same color for carbon.

6. The acid concentration is not critical, and the same amount of acid can be used for all percentages of carbon.

7. Only one minute of heating with nitric acid is required to develop the carbon color.

8. The color is stable for three hours without change.

In the proposed method the sample of titanium is dissolved in a mixture of sulfuric and fluoboric acids. Nitric acid is them added to dissolve the titanium carbide. The solution is boiled and filtered, and the yellow color is read with a spectrophotometer. The spectrophotometric curves obtained for the color are shown in Fig. 1. It is seen that the maximum absorption occurs around 415 millimicrons, but a greater sensitivity is obtained at a higher wavelength. It was decided, therefore, to read the color at 450 millimicrons. The calibration curve obtained at 450 millimicrons, using a series of titanium samples whose carbon content had been determined by combustion, is shown in Fig. 2. Elements present in titanium metal (oxygen, nitrogen, small amounts of tungsten

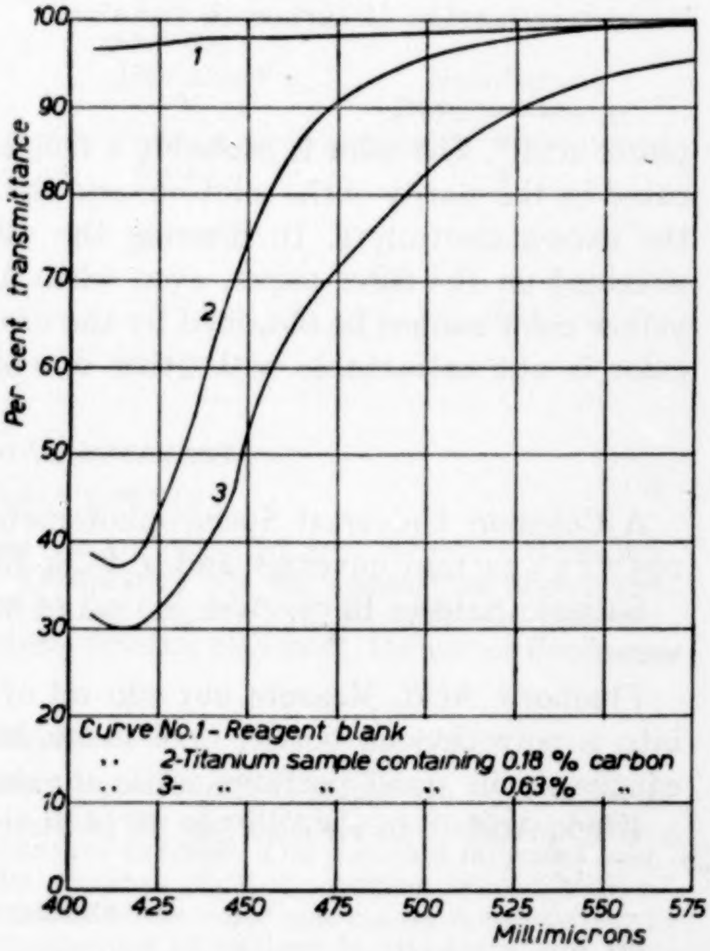

Fig. 1. Spectrophotometric curves for the colorimetric determination of carbon in titanium.

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and manganese, and up to 0.3 per cent iron, silicon and magnesium) do not interfere. The method is designed for titanium containing up to 0.7 per cent carbon. The procedure is very rapid and is readily adaptable to the determination of carbon in a large number of samples at the same time. There is no danger of loss of hydrocarbons in dissolving the sample in a non-oxidizing acid, since titanium carbide is not attacked by any acid except nitric acid[8].

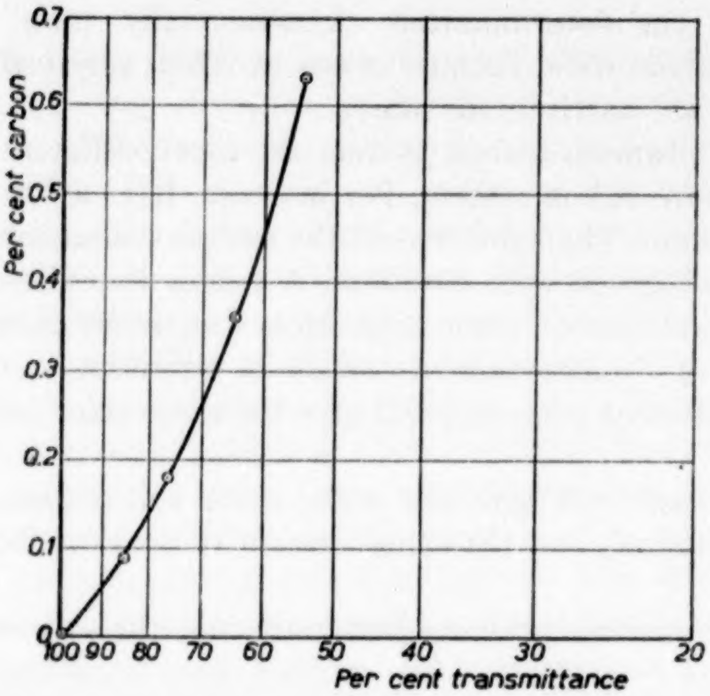

Fig. 2. Calibration curve for the colorimetric determination of carbon in titanium.

The chemistry of the yellow coloration is obscure. It is probably a nitrated organic complex[9,10]. It has been assigned the formula $C_{22}H_{17}(NO_2)O_{11}$ (nitrographitic acid)[9]. The color is probably a true color rather than a colloid. This is indicated by the clarity of the solutions and the stability of the color in the presence of the excess electrolyte. In filtering the solution a yellow coloration was never obtained on the filter paper, even when a very fine filter paper was used. The yellow color cannot be obtained by the use of any other acid but nitric acid. The color is not extractable with ether or chloroform.

APPARATUS AND REAGENTS

A Coleman Universal Spectrophotometer, Model 14, with optically matched 105×13×13 mm cuvettes and a PC-4 filter.

Sulfuric Acid (1 to 3). Add 300 ml of sulfuric acid (sp. gr. 1.84) to 900 ml of water.

Fluoboric Acid. Measure out 280 ml of hydrofluoric acid (48 to 50 per cent.) into a polyethylene bottle. Cool in an ice bath. Add 130 grams of boric acid cautiously in small portions while shaking.

Nitric Acid (1 to 1). Add 500 ml of nitric acid (sp. gr. 1.41) to 500 ml of water.

PROCEDURE

Transfer a 1 gram sample to a covered 250 ml beaker and add 20 ml of sulfuric acid (1 to 3) and 10 ml of fluoboric acid. Warm on the hot plate until the sample is dissolved. Remove the beaker from the hot plate and wash down the cover

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lid and sides in order to remove any adhering particles of titanium carbide. Add slowly 5 ml of nitric acid (1 to 1) while swirling the beaker. Place the beaker on the hot plate with the cover lid ajar. Heat to boiling and boil for one minute (no longer). Cool in a running water bath for a few minutes. Filter through a medium texture filter paper (Whatman No. 40) into a 50 ml volumetric flask and wash with water. Dilute to the 50 ml mark and shake. Compare colorimetrically with a reagent blank at 450 millimicrons. Convert the readings to per cent. carbon by consulting a calibration curve prepared from titanium samples whose carbon content has been determined by combustion.

The results obtained colorimetrically for carbon for four samples of titanium are shown in Table I. The results compare well with the results obtained by combustion.

TABLE I

RESULTS FOR THE COLORIMETRIC DETERMINATION OF CARBON IN TITANIUM

Carbon Present % *	Average Carbon Found Colorimetrically %	Standard Deviation %	Number of Determinations
0.090	0.087	0.012	6
0.180	0.190	0.009	6
0.361	0.360	0.015	7
0.632	0.627	0.020	7

* As determined by combustion.

ACKNOWLEDGEMENTS

The authors are indebted to WILLIAM A. DUPRAW of the Armour Research Foundation of the Illinois Institute of Technology for his suggestion about the use of fluoboric acid. The authors originally used a nitric-hydrofluoric acid mixture to dissolve the samples and obtained excellent results. However, the use of fluoboric acid is more convenient.

SUMMARY

A method is proposed for the colorimetric determination of carbon in titanium. In the method the sample is dissolved in a mixture of sulfuric and fluoboric acids, and nitric acid is added to dissolve the titanium carbide. The solution is boiled and filtered, and the yellow coloration from the nitrated organic complex is read with a spectrophotometer. A spectrophotometric study of the color was made. A comparison was made between the colorimetric determination of carbon in titanium and the colorimetric determination of carbon in steels. The proposed method is rapid and is readily adaptable to the determination of carbon in a large number of samples at one time. The procedure is designed for titanium containing up to 0.7 per cent. carbon. None of the elements encountered in "commercially pure" titanium metal interferes.

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RÉSUMÉ

Une méthode est proposée pour le dosage colorimétrique du carbone dans le titane. L'échantillon est dissous dans un mélange d'acides sulfurique et fluoborique, et l'acide nitrique est ajouté pour dissoudre le carbure de titane. La solution est portée à ébullition et filtrée; la coloration jaune du composé nitré formé est mesurée au spectrophotomètre. Une étude spectrophotométrique de la coloration est effectuée ainsi qu'une comparaison entre le dosage colorimétrique du carbone dans le titane et le dosage colorimétrique du carbone dans les aciers. La méthode proposée est rapide, et permet de doser le carbone dans un grand nombre d'échantillons; elle convient pour des titanes renfermant jusqu'à 0.7% de carbone. Aucun des éléments pouvant être présents dans le titane ,,commercialement pur" gêne.

ZUSAMMENFASSUNG

Es wird eine Methode zur kolorimetrischen Bestimmung von Kohlenstoff in Titan vorgeschlagen. Bei der Methode wird die Probe in einer Mischung von Schwefelsäure und Fluorborsäure gelöst und Salpetersäure wird zur Lösung des Titankarbids hinzugefügt. Die Lösung wird gekocht und filtriert und die gelbe Färbung des nitrierten organischen Komplexes wird in einem Spektrophotometer abgelesen. Eine spektrometrische Untersuchung der Farbe wurde durchgeführt und die kolorimetrische Bestimmung von Kohlenstoff in Titan mit der kolorimetrischen Bestimmung von Kohlenstoff in Stählen verglichen. Die vorgeschlagene Methode ist schnell und leicht zur Bestimmung von Kohlenstoff in einer grossen Anzahl von Proben zu gleicher Zeit anwendbar. Das Verfahren ist für Titan, das bis zu 0.7% Kohlenstoff enthält, bestimmt. Keines der in ,,handelsüblich reinen" Titanmetallen vorhandenen Ionen stören.

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COLORIMETRIC DETERMINATION OF NIOBIUM IN TITANIUM ALLOYS

by

GEORGE NORWITZ, MAURICE CODELL AND FRANK D. VERDERAME

Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa. (U.S.A.)

INTRODUCTION

The determination of niobium in titanium alloys proved to be an extremely difficult analytical problem. Previous investigators[29,33,49,62,78] have pointed out the complexities of the problems involved in the determination of niobium in the presence of relatively small amounts of titanium. In the presence of the amounts of titanium found in titanium alloys the difficulties are much increased.

A few preliminary experiments clearly indicated that before niobium in titanium alloys could be determined, it would first have to be separated from the bulk of the titanium. Various separations were tried. The hydrolysis of the niobium by boiling a dilute hydrochloric or sulfuric acid solution[23,24,38,66,77] containing the niobium and titanium could not be applied. When the solution was not acid enough the titanium hydrolyzed with the niobium. When the solution was too acid, no precipitate at all appeared because of the solvent action of titanium on the niobium[29,33,62]. This solvent action is shown by a simple experiment devised in this laboratory. 0.1 gram of niobium metal was dissolved in a mixture of hydrofluoric and nitric acids, 2 ml of sulfuric acid were added and the solution evaporated to fumes of sulfuric acid. On dilution to 100 ml with water, the niobium immediately hydrolyzed. 0.1 gram of niobium metal and 0.1 gram of titanium metal were dissolved in a mixture of hydrofluoric and nitric acids, 2 ml of sulfuric acid were added and the solution evaporated to fumes of sulfuric acid as before. On dilution to 100 ml with water, the solution remained clear indefinitely.

Niobium has been separated by fuming with perchloric acid[52,76]. Such a procedure is not applicable to titanium alloys because of the precipitation of titanium. A method much used for the determination of niobium is to add an excess of sulfurous acid to hydrochloric, sulfuric or perchloric acid solution of the sample and then boil[8,21,26,38,87,88]. The sulfurous acid acts as a buffer and also reduces contamination by iron by keeping the iron in the ferrous state. The method is not applicable to titanium alloys because the sulfurous acid causes hydrolysis of the titanium. Niobium has been separated from titanium by boiling a solution containing hydrochloric and tartaric acid[65,75], or nitric and tartaric acid[68,70]. The method gave incomplete recovery of niobium when applied to titanium alloys. It is known that niobium can be separated as insoluble sodium columbate from a solution saturated with sodium chloride[64,69,73]. The method was not applicable to titanium alloys because of precipitation of titanium. The use of pyrogallol to separate the niobium from a dilute acid solution[1,2,3,5,6] was not found to be applicable in the presence of large amounts of titanium. The use of the bicarbonate separation of the niobium[64,86], or the sodium hydroxide separation of niobium[19,44], or the ammoniacal separation of niobium[19,44], or the ammoniacal-magnesia separation of niobium[57] was not applicable to titanium alloys because of precipitation of the titanium. Hexamethylenetetramine and similar amines will quantitatively precipitate niobium[85]. However, titanium is also precipitated.

A method has been proposed[82] in which a dilute sulfuric acid solution of the niobium and titanium is treated with zinc amalgam to reduce the titanium. Ammonium acetate is then added and the niobium hydrolyzed. Most of the titanium remains in solution. The method was not applicable to the amounts of titanium found in titanium alloys. Niobium has been precipitated by 8-hydroxyquinoline[81] but titanium also precipitates. Both niobium[15,19,20,45,50,51,74,80] and titanium[14,20,79] are precipitated by cupferron. However, it is known that niobium cupferride is not extracted by chloroform in the absence of excess hydrogen cupferrate[20]. In this respect niobium cupferride differs from titanium cupferride, which is readily extracted under these conditions[20,47]. This difference in behavior of niobium and titanium cupferrides was investigated as a possible means of separating niobium from titanium. It was found that if titanium was present considerable niobium was extracted with the titanium. Benzene arsonic acid and similar acids will precipitate niobium[2,3,4,6,34,59] but titanium is also precipitated. If hydrogen peroxide is added, the titanium can be kept in solution. However, under these circumstances the niobium remains in solution when large amounts of titanium are present. The chlorination of niobium and titanium with octachloropropane, and subsequent distillation of the titanium chloride[9,33,56] was not considered to be a promising procedure for titanium alloys, since the chlorination of titanium does not work well unless a significant amount of niobium is present as in niobium ores[33,56]. Also, before the method could be applied it would be necessary to remove any iron present, since iron catalytically decomposes the octachloropropane[33,56]. Salicylic acid has been used for the separation of niobium from titanium[31,48,68,70,71]. It was found in this laboratory that the method did not give good results for large amounts of titanium. Niobium has been determined on solid specimens of ferrous alloys by the use of X-ray fluorescence[10,13,43] and by spectroscopy[27,28,55,61]. These methods can not at present be applied to titanium alloys because there is no accurate method for determining the niobium content of a series of standards that would be needed.

Tannin has been used for the separation of niobium from titanium using a dilute sulfuric acid medium[67,75], a dilute hydrochloric acid medium[33,78], or a boric-hydrofluoric acid medium[11,12]. It was found in this laboratory that the boric-hydrofluoric acid medium gave the best results. BYKOVA[11,12] applied the boric-hydrofluoric acid medium to the gravimetric determination of niobium and tantalum in 0.2 to 0.3 gram of mixed oxides containing niobium, tantalum and titanium. By somewhat modifying the procedure, it was found that the method could be applied to the separation of niobium from all but a small fraction of 0.5 gram of titanium. The method as finally adopted consisted of dissolving the titanium and niobium in a mixture of hydrofluoric and nitric acids, evaporating to a small volume, adding tannin, hydrochloric acid and boric acid, boiling and allowing the solution to stand overnight. The precipitate was filtered, boiled with a hydrochloric acid solution containing tannin, allowed to stand two hours and again filtered. The method was checked by igniting to the oxide and correcting for occluded titanium colorimetrically.

Experiments with the above method led to the following conclusions:

1. The acidity is moderately critical. If the solution is not acid enough, too much titanium precipitates. If the solution is too acid, the precipitation of the niobium is incomplete.
2. The acid concentration cannot be adjusted by neutralizing the excess acid with ammonium hydroxide. Low results were obtained for niobium when this technique was adopted.
3. The solution must stand overnight after the first separation to obtain complete precipitation of the niobium.
4. The solution need stand only two hours after the second separation to obtain quantitative precipitation of the niobium.
5. The addition of the boric acid for the first tannin separation is essential in order to tie up the fluoride ion. If the boric acid is not added, very low results for niobium will be obtained. Apparently, the niobium forms a very stable complex with fluoride that cannot be readily broken up by tannin.
6. The addition of two grams of tannin is necessary for the first separation. If only one gram of tannin is used, low results for niobium will be obtained. The amount of tannin required for the second separation is not critical.
7. About 0.05 to 0.15 gram of titanium is precipitated in the first tannin separation, depending on the amount of niobium present.
8. The amount of titanium occluded after the second separation is approximately equal to the amount of niobium present.

A satisfactory separation of niobium from the bulk of the titanium having been achieved by the above tannin procedure, the next step was the determination of the niobium. The use of a gravimetric procedure whereby the precipitate is ignited to the oxide and a correction made for the titanium is only useful in the absence of such metals as tantalum, tungsten, molybdenum, iron and vanadium.

The determination of the niobium in the ignited precipitate by reduction with a Jones reductor followed by titration[19,32,37] was of no value because many other elements that might be present in the tannin precipitate, such as titanium, tungsten, molybdenum, iron and vanadium, would also be reduced and titrated. The use of a colometric procedure for the determination of the niobium was therefore considered to be the best approach. Various colorimetric reagents for niobium have been proposed. The peroxide method by which a yellow color is obtained on the addition of hydrogen peroxide to a concentrated sulfuric acid, or a concentrated sulfuric acid and phosphoric acid solution of niobium[21,35,36,83,84] was not too satisfactory. The method was not very sensitive and the correction required for the titanium was too high. The brownish color obtained by reducing a hydrofluoric acid[46] or a phosphoric acid solution[22] of the niobium with zinc has been used for the colorimetric estimation of niobium. Such a procedure was subject to too much interference from such elements as titanium and tungsten which give interfering colors. The use of pyrogallol in alkaline solution as a colorimetric reagent for niobium[25,39,40,41,53,54,60] was found to be unsatisfactory. The yellow color obtained is insensitive, it is subject to too much interference from titanium and a very high blank is obtained.

The best colorimetric procedure for the determination of niobium seemed to be the thiocyanate method. The yellow color can be extracted with ether[7,42] or developed in a water-acetone medium[18]. It was decided to use the latter type of medium. The method as finally adopted was essentially the method described by FREUND AND LEVITT[18]. The color is read at 420 millimicrons instead of at 385 millimicrons (the point of maximum absorption) in order to reduce the interference from tantalum. The latter metal gives a visually colorless complex with thiocyanate that shows absorption at 385 millimicrons[18]. It is necessary that the reagents used in the thiocyanate method be measured out accurately[18]. Tartaric acid is used in the method to keep niobium and tantalum in solution. The intensity of the thiocyanate color is somewhat dependent upon the amount of tartaric acid present. Therefore, it is necessary to add sufficient blank solution containing tartaric acid to bring the volume up to 10 ml, when aliquots smaller than 10 ml are taken. The color is also somewhat dependent on the sulfate concentration[18]. However, the same result for niobium was obtained whether 2.5 grams or 5 grams of potassium bisulfate were used to fuse the niobium oxide. This was not unexpected since the table shown by FREUND AND LEVITT[18] for sulfate interference shows the same absorbancy reading for samples containing 0.0006 and 0.0078 moles per liter of sulfate.

There is no danger of volatilizing niobium as the fluoride when the sample is dissolved in hydrofluoric and nitric acids, and evaporated to a small volume[12,30,89]. The use of a nitric-hydrofluoric acid mixture is by far the best medium for dissolving a niobium-titanium alloy. It is well known that metallic niobium and binary metallic compounds of niobium are easily soluble in this acid mixture[19,58,72].

The method proposed in this paper is reasonably rapid. Six determinations can be finished in two days. This is a big saving in time when compared to previous methods for the determination of niobium in the presence of titanium that require several days. The method is designed for titanium alloys containing 0.05 to 10 per cent. niobium.

APPARATUS AND REAGENTS

Coleman Universal Spectrophotometer, Model 14, with optically matched 13×13×105 mm cuvettes and a PC-4 filter.

Hydrochloric Acid, sp. gr. 1.18

Hydrochloric Acid (2 to 1). Mix 1000 ml of hydrochloric acid and 500 ml of water

Hydrofluoric Acid, 50 per cent.

Nitric Acid, sp. gr. 1.42

Sulfuric Acid, sp. gr. 1.84

Tannin (Tannic Acid) cp

Tannin Wash Solution. Add 5 grams of tannin and 25 ml of hydrochloric acid to 1 liter of water. Make fresh daily.

Tartaric Acid Solution (1.2*M*). Dissolve 450 grams of cp tartaric acid in water and dilute to 2.5 liters with water.

Stannous Chloride Solution (2*M*). Dissolve 113 grams of cp $SnCl_2.2H_2O$ in about 200 ml of hydrochloric acid. Dilute to 250 ml with hydrochloric acid.

Potassium Thiocyanate Solution (3*M*). Dissolve 292 grams of cp potassium thiocyanate in water and dilute to 1 liter with water.

Acetone, cp

Boric Acid, cp

Potassium Bisulfate, fused lumps, cp

Standard Niobium Solution No. 1 (1 ml = 0.020 mg of niobium). Fuse 0.05724 gram of Nb_2O_5 (A. D. Mackay & Co., New York) in a platinum crucible with 10 grams of potassium bisulfate. Transfer the crucible and melt to a 1 liter beaker containing 800 ml of tartaric acid solution (1.2*M*). Warm gently on the hot plate with frequent stirring until the melt has dissolved. Wash down and remove the crucible. Cool and dilute to 2 liters in a volumetric flask.

Standard Niobium Solution No. 2 (1 ml = 1.00 mg of niobium). Transfer 1.0000 gram of niobium metal (A. D. Mackay & Co., New York) to a covered 30 ml platinum crucible, and add 5 ml of water. Add hydrofluoric acid and nitric acid dropwise to dissolve the niobium. Use about 5 drops of hydrofluoric acid to 1 drop of nitric acid. When the niobium has dissolved, wash down the cover lid and remove it. Warm the crucible on the hot plate for a few minutes. Cool. Add 20 ml of hydrofluoric acid and wash into a beaker containing 400 ml of water and 25 ml of sulfuric acid. Dilute to 1 liter in a volumetric flask.

Standard Tantalum Solution (1 ml = 1.00 mg of tantalum). Dissolve 1.0000 gram of tantalum metal (A. D. Mackay & Co., New York) as described above, wash into a beaker containing 400 ml of water and 40 ml of sulfuric acid, and dilute to 1 liter in a volumetric flask.

Blank Solution. Fuse 5 grams of potassium bisulfate in a platinum crucible. Cool. Transfer the crucible and melt into a beaker containing 400 ml of tartaric acid solution (1.2*M*). Warm on the hot plate until the melt has dissolved. Wash down and remove the crucible. Cool, and dilute to 1 liter in a volumetric flask.

METHOD

Preparation of calibration curve

Add to 50 ml volumetric flasks the following aliquots of Standard Niobium Solution No. 1: 1 ml, 2 ml, 3 ml, 5 ml, 7 ml, 8 ml and 10 ml. Add from a burette enough Blank Solution to bring the volume up to 10 ml. Add in order the following reagents measured with pipettes: 15 ml of hydrochloric acid (2 to 1), 1 ml of 2*M* stannous chloride solution, and 10 ml of acetone. Cool in a water bath at 20° C for 15 minutes. Add from a pipette 10 ml of 3*M* potassium thiocyanate solution. Dilute almost to the 50 ml mark with water and return the volumetric flasks to the water bath for 5 minutes. Remove the flasks from the water bath and dilute to the 50 ml mark with water. Allow to stand 15 minutes and compare the color at 420 millimicrons with a reagent blank. Plot the per cent. transmittance against the milligrams of niobium. The calibration curve obtained by the authors is shown in Figure 1.

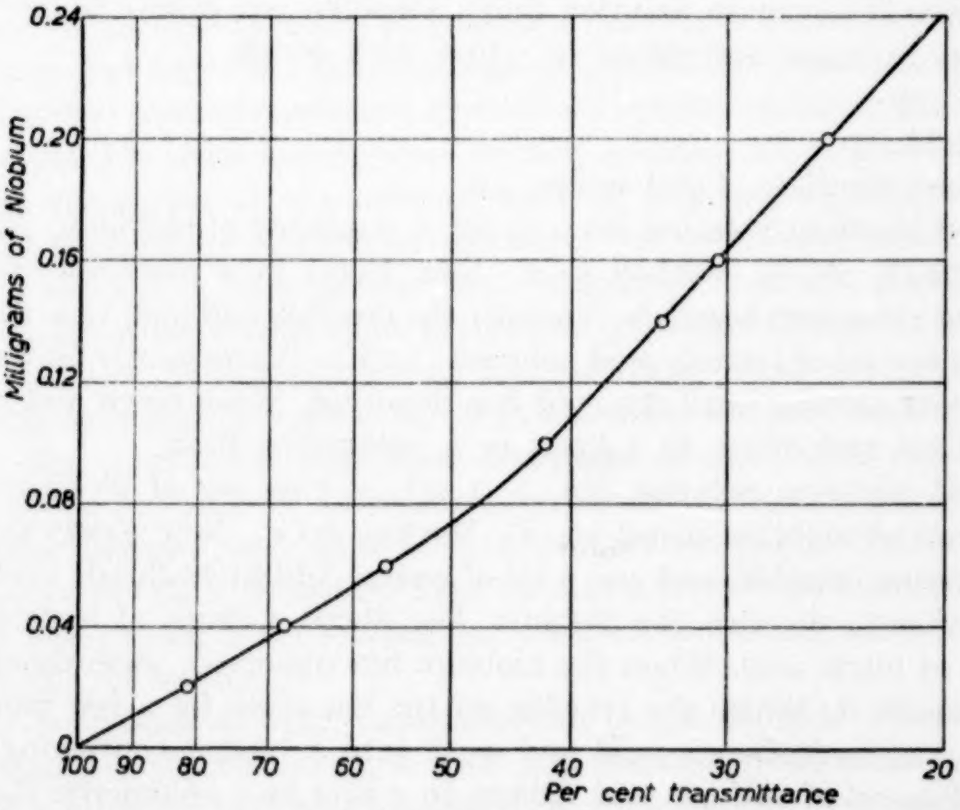

Fig. 1. Calibration curve for the colorimetric determination of niobium in titanium alloys.

References p. 572-574.

Procedure

Transfer 0.5 gram of the sample to a covered 30 ml platinum crucible, and add 5 ml of water. Add hydrofluoric acid and nitric acid dropwise to dissolve the sample. Use about 5 drops of hydrofluoric acid to 1 drop of nitric acid. Enough nitric acid should be present at the end of the reaction to ensure that the titanium is oxidized to the titanic state. If the reaction becomes too violent, add a little water from a wash bottle. After the reaction is complete, wash down the cover lid and remove it. Heat over an asbestos pad on a hot plate until the volume is reduced to about 3 ml. Remove from the hot plate and allow to cool to room temperature. Add 3 ml of water and 3 ml of hydrochloric acid. Wash the contents of the crucible into a 600 ml beaker containing 100 ml of water and 2 grams of tannin. Add 2 ml of water and 2 ml of hydrochloric acid to the crucible. Swab the crucible with a policeman and wash the contents into the 600 ml beaker. Add 8 grams of boric acid to the 600 ml beaker and stir. Dilute to 250 ml with water, cover with a watch glass, and boil moderately for 10 minutes. Remove from the hot plate and allow to stand overnight. Filter through a medium texture filter paper (Whatman No. 40) and wash with Tannin Wash Solution. Add 240 ml of water, 10 ml of hydrochloric acid and 2 grams of tannin to the 600 ml beaker. Transfer the filter paper and precipitate to the beaker and break up the filter paper with a stirring rod. Cover with a watch glass and boil moderately for 15 minutes. Remove from the hot plate and allow to stand for 2 hours. Filter through a medium texture filter paper (Whatman No. 40) and wash with Tannin Wash Solution. Place the filter paper and precipitate into a platinum crucible. Drive off the moisture by heating the crucible on the hot plate. Char and burn off the filter paper by igniting at low heat. Finally, ignite at red heat for a few minutes. Add potassium bisulfate and fuse. For samples containing less than 5 per cent. niobium use 2.5 grams of potassium bisulfate; for samples containing 5 to 10 per cent. niobium use 5 grams of potassium bisulfate. Allow the crucible to cool to room temperature. Transfer the crucible and melt to a 400 ml beaker containing 200 ml of $1.2M$ tartaric acid solution. Warm gently on the hot plate with frequent stirring until the melt has dissolved. Wash down the crucible and remove it. Allow to cool, transfer to a 500 ml volumetric flask and dilute to the mark with water.

Transfer an aliquot of the solution to a 50 ml volumetric flask. For samples containing less than 1 per cent. niobium use a 10 ml aliquot. For samples containing more than 1 per cent. niobium use an aliquot containing about 0.06 to 0.16 mg of niobium. For instance, for samples containing 2 per cent. niobium use a 5 ml aliquot; for samples containing 5 per cent. niobium use a 2 ml aliquot; for samples containing 10 per cent. niobium use a 1 ml aliquot. When measuring the 1 ml aliquot use a 1 ml pipette graduated into tenths. When an aliquot of less than 10 ml is used, add enough Blank Solution, measured from a burette, to bring the volume up to 10 ml.

Add in order by means of pipettes the following reagents: 15 ml of hydrochloric acid (2 to 1), 1 ml of $2M$ stannous chloride solution, and 10 ml of acetone. Cool in a water bath at 20° C for 15 minutes. Add from a pipette 10 ml of $3M$ potassium thiocyanate solution. Dilute almost to the 50 ml mark with water and return to the water bath for 5 minutes. Dilute to 50 ml mark with water. Allow to stand 15 minutes and compare colorimetrically at 420 millimicrons with a reagent blank. Convert the readings to milligrams of niobium by consulting the calibration curve. Calculate the per cent. niobium by use of the following formula:

$$\text{Per cent. Niobium} = \frac{\text{mg of Niobium as Read from Curve}}{\text{mg of Sample in Aliquot}} \times 100$$

RESULTS AND DISCUSSION

The results obtained on synthetic samples prepared by adding Standard Niobium Solution No. 2 to pure titanium metal are shown in Table I. The results obtained for niobium in the presence of possible interferences are shown in Table II. It is seen that the presence of tantalum can cause two opposing tendencies. Tantalum can cause high results for niobium because it forms a complex that absorbs somewhat even at 420 millimicrons. Tantalum can cause low results for niobium by hindering the development of the niobium color. The resultant effect of the tantalum depends upon the amount of tantalum present, the amount of niobium present, and the ratio of tantalum to niobium. FREUND AND LEVITT[18] have indicated that the presence of tantalum can cause both high and low results for niobium. LAUW-ZECHA, LORD AND HUME[42] in their ether extraction procedure found only a tendency towards low results. It is difficult to explain the repressive action of tantalum on the niobium color. The effect does not seem to be due to the hydrolysis of the tantalum with subsequent absorption of the niobium, since the solutions remained very clear. Possibly the effect is due to the masking effect of tantalum on niobium that has been described by SCHOELLER[62]. In other words, tantalum and niobium may form some kind of complex.

TABLE I

RESULTS FOR NIOBIUM IN SYNTHETIC SAMPLES OF TITANIUM ALLOYS

Niobium Added (%)	Average Niobium Found (%)	Standard Deviation (%)	No. of Determinations
0.050	0.050	0.004	6
0.200	0.213	0.008	6
1.00	0.991	0.023	6
2.00	1.98	0.059	5
5.00	5.02	0.075	5
10.00	10.07	0.24	6

TABLE II

RESULTS FOR NIOBIUM IN THE PRESENCE OF POSSIBLE INTERFERENCES

Element	Amount Added (%)	Added As	Niobium Added (%)	Niobium Found (%)
Tantalum	5.0	Standard Tantalum Solution	0	0.06
,,	5.0	,,	0	0.06
,,	1.0	,,	0.20	0.22
,,	1.0	,,	0.05	0.06
,,	0.5	,,	1.00	0.98
,,	0.5	,,	1.00	1.00
,,	1.0	,,	1.00	0.90
,,	1.0	,,	1.00	0.84
,,	1.0	,,	2.00	1.86
,,	2.0	,,	5.00	4.95
,,	0.8	,,	2.00	2.02
Tungsten	5.0	$Na_2WO_4.2H_2O$	1.00	1.17
,,	1.0	,,	1.00	1.02
,,	1.0	,,	0.20	0.21
Molybdenum	10.0	$(NH_4)_6Mo_7O_{24}.4H_2O$	1.00	0.99
,,	10.0	,,	0.20	0.20
Iron	10.0	$FeCl_3.6H_2O$	1.00	0.97
,,	10.0	,,	0.20	0.22
Chromium	10.0	$Cr_2(SO_4)_3$	1.00	1.03
,,	10.0	,,	0.20	0.19
Vanadium	5.0	$(VO)_2Cl_4$	1.00	1.00
,,	5.0	,,	0.20	0.21
Manganese	10.0	$MnSO_4.H_2O$	1.00	1.02
Silicon	5.0	$Na_2SiO_3.9H_2O$	1.00	0.98
Cobalt	5.0	$CoCl_2.6H_2O$	1.00	0.97
Copper	5.0	$CuSO_4.5H_2O$	1.00	0.97
Nickel	5.0	$NiCl_2.6H_2O$	1.00	0.97
Tin	5.0	$SnCl_2.2H_2O$	1.00	1.01
Magnesium	5.0	$MgSO_4.7H_2O$	1.00	1.00
Calcium	5.0	$CaSO_4.2H_2O$	1.00	1.00
Aluminium	5.0	$Al_2(SO_4)_3.18H_2O$	1.00	1.03
Boron	1.0	H_3BO_3	1.00	0.99
Phosphorus	1.0	$(NH_4)_2HPO_4$	1.00	1.02
,,	1.0	,,	0.20	0.19

For titanium alloys containing less than 1 per cent. niobium the recommended limit for tantalum is 0.5 per cent. For alloys containing more than 1 per cent. niobium the recommended limit for tantalum is 0.4 the amount of niobium. present. Tungsten is not precipitated by tannin in the absence of niobium. However, if niobium is present, some tungsten is precipitated. If several per cent. tungsten is present, together with significant amounts of niobium, the interference from tungsten will be very appreciable, as can be seen from Table II. The recommended limit for tungsten is 1 per cent. Small amounts of iron, molybdenum, chromium and vanadium are occluded by the tannin precipitate. However, these amounts of iron, molybdenum, chromium and vanadium in no way affect the niobium color. No interference was encountered from silicon, manganese, cobalt, copper, nickel, tin, magnesium, calcium, aluminum and boron. None of these elements, with the possible exception of silicon, would be expected to be occluded by the tannin precipitate to any appreciable extent. The fact that 1 per cent. phosphorus does not interfere with the method indicates that the tannin precipitation provides a very good separation of niobium from phosphorus, since phosphate can hinder the development of the niobium color[18]. The amount of titanium that is occluded after two tannin separations has no effect on the niobium color.

The indicated limits of possible interfering elements is above the nominal amounts of these elements that would be found in commercial titanium alloys. Should the occasion arise, the limits could be extended by use of a 0.25 gram sample instead of a 0.5 gram sample. For instance, this laboratory was recently called on to analyze a special experimental titanium alloy containing approximately 1 per cent. niobium and 1 per cent. tantalum. The results obtained for niobium, when the sample was run 6 times using a 0.25 gram sample, are shown in Table III.

TABLE III

RESULTS FOR NIOBIUM IN A SPECIAL NIOBIUM-TANTALUM-TITANIUM ALLOY CONTAINING APPROXIMATELY ONE PER CENT NIOBIUM AND ONE PER CENT. TANTALUM

	Niobium Found (%)
	0.96
	0.94
	0.94
	0.94
	0.96
	0.92
Average (%)	0.943
Standard Deviation (%)	0.015

A few experiments showed that tantalum is quantitatively precipitated with the niobium by the tannin procedure described in this paper. This was to be expected[11,12]. If weighable amounts of tantalum are present, and if only titanium, tantalum and niobium are present in the alloy, a fair result for tantalum can be obtained by igniting the tannin precipitate to the oxide and correcting for the titanium and the niobium. However, if the amount of tantalum present is small, and if such elements as tungsten, iron, molybdenum, chromium, vanadium and silicon are present, the determination of tantalum by difference is subject to obvious errors.

References p. 572-574.

Tannin (also known as tannic acid, or gallo-tannic acid, or digallic acid) is a collective name for a water-soluble mixture of compounds found in certain plant materials. It consists of ester-like compounds of various sugars with phenolcarboxylic acid. The chief constituent of tannin is probably pentagalloyl-glucose. The mechanism involved in the use of tannin as a precipitating reagent for niobium and other metals has not been definitely established. According to the SCHOELLER school[63], the reaction consists of mutual discharge and coagulation of the positively charged particles of the hydrous oxide by the negatively charged particles of the tannin. FEIGL[16,17], however, has pointed out that the reaction is probably much more complicated. The process may consist of the elimination of water through condensation of basic OH groups of the hydrous oxide particles with the phenolic hydroxyl groups of the tannin particles[17]. The resultant absorption compound between the oxide and the tannin particles is less soluble than the oxide or tannin itself. The tannin binding takes place on the surface. The precipitate is not homogeneous, nor does it correspond to a definite chemical formula.

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SUMMARY

There is need for a method for the determination of niobium in titanium alloys, since niobium-titanium alloys are becoming increasingly important. The determination of niobium in this type of alloy is an extremely difficult matter. Many approaches were tried before the problem was solved. In the method proposed in this paper the sample is dissolved in a mixture of hydrofluoric and nitric acids, the solution evaporated to a small volume, and boric acid added. Two tannic acid separations are then made to separate the niobium from the bulk of the titanium. The niobium is determined colorimetrically by the thiocyanate method using a water-acetone medium. A study was made of the possible interference of elements that might be present in titanium alloys. It was found that the presence of tantalum causes two opposing tendencies. Tantalum can cause high results for niobium because it forms a complex with thiocyanate which is visually colorless but shows some absorption. Tantalum can cause low results for niobium by hindering the development of the niobium color. The resultant effect of the tantalum depends upon the amount of tantalum present, the amount of niobium present and the ratio of tantalum to niobium. The presence of more than one per cent. tungsten can lead to high results for niobium. Other elements that might be present in titanium alloys do not interfere with the method. The procedure is designed for titanium alloys containing 0.05 to 10 per cent. niobium. The method is reasonably rapid. Six determinations can be finished in two days. The method should be applicable to many other materials besides titanium alloys.

RÉSUMÉ

Il est nécessaire d'avoir une méthode de dosage du niobium dans les alliages de titane, les alliages niobium-titane devenant de plus en plus importants. Le dosage du niobium dans ce type d'alliages est très difficile. Plusieurs essais ont été effectués

avant de résoudre ce problème. Dans la méthode proposée dans cet article, l'échantillon est dissous dans un mélange d'acides fluorhydrique et nitrique, la solution est évaporée à un faible volume et additionnée d'acide borique. On effectue ensuite 2 séparations à l'acide tannique pour séparer le niobium du titane. Le niobium est dosé colorimétriquement par la méthode au thiocyanate dans un millieu eau-acétone. Une étude a été faite sur les interférences possibles des éléments qui peuvent être présents dans les alliages au titane. La présence de tantale peut présenter 2 tendances opposées: donner des résultats trop forts pour le niobium, Ta formant un complexe avec le thiocyanate, apparemment incolore mais présentant une certaine absorption; donner des résultats trop faibles pour le niobium, Ta empêchant le développement de la coloration du niobium. L'effet résultant dépend de la teneur en tantale, en niobium et du rapport tantale/niobium. La présence de plus de 1% de tungstène peut conduire à des résultats élevés pour le niobium. D'autres éléments, pouvant être présents dans les alliages de titane, gênent. Ce procédé est indiqué pour des alliages de titane renfermant 0.05 à 10% de niobium. La méthode est d'une rapidité convenable. Six dosages peuvent être appliqués à de nombreux types de substances, autres que les alliages du titane.

ZUSAMMENFASSUNG

Es ist ein Bedarf für eine Methode zur Bestimmung von Niob in Titanlegierungen vorhanden, seit Niob-Tantallegierungen an Wichtigkeit zunehmen. Die Bestimmung von Niob in Legierungen dieser Art ist eine äusserst schwierige Angelegenheit. Viele Versuche zu ihrer Lösung wurden durchgeführt bevor das Problem gelöst wurde. Bei der in dieser Arbeit vorgeschlagenen Methode wird die Probe in einer Mischung von Flussäure und Salpetersäure gelöst, die Lösung auf ein kleines Volumen eingedunstet und Borsäure hinzugefügt. Dann werden zwei Tanninsäuretrennungen durchgeführt, um Niob von der Hauptmenge des Titans abzutrennen. Niob wird mit der Thiocyanatmethode unter Benützung einer Wasser-Aceton-Lösung kolorimetrisch bestimmt. Es wurde eine Untersuchung der möglicherweise störend wirkenden Elementen durchgeführt, die in Titanlegierungen vorhanden sein können. Es wurde gefunden dass die Gegenwart von Tantal zwei entgegengesetzte Wirkungen hervorruft. Es kann zu hohe Niobresultate verursachen, da es mit Thiocyanat einen Komplex bildet, der farblos erscheint, aber einige Absorption zeigt. Es kann zu niedrige Niobwerte verursachen, da es die Entwicklung der Niobfarbe hemmt. Die resultierende Wirkung des Tantals hängt von der Menge des vorliegenden Tantals, der Menge des vorliegenden Niobs und dem Verhältnis von Niob zu Tantal ab. Die Anwesenheit von mehr als 1% Wolfram kann zu zu hohen Resultaten für Niob führen. Andere Elemente, die in Titanlegierungen anwesend sein können, stören die Methode nicht. Dies Verfahren ist bestimmt für Titanlegierungen mit einem Gehalt von 0.05-10% Niob. Die Methode geht verhältnismässig schnell. Sechs Bestimmungen können in zwei Tagen durchgeführt werden. Die Methode würde ausser auf Titanlegierungen auch auf viele andere Materialien anwendbar sein.

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THE SPECTROPHOTOMETRIC DETERMINATION OF AMMONIA IN NATURAL WATERS WITH PARTICULAR REFERENCE TO SEA-WATER

by

J. P. RILEY

Department of Oceanography, The University of Liverpool (England)

A knowledge of the ammonia content of sea-water is of considerable value in the study of the nitrogen cycle in the oceans. The concentration of ammonia in ocean water is always low, varying from less than 5 mg/m^3 up to 50 mg NH_4-N/m^3, depending upon the season, position, and depth[1], a minimum concentration being encountered at the time of the spring outburst of plankton growth. The ammonia in the sea is mainly derived from the excretions of marine animals and from the breakdown of organic nitrogen compounds and amino acids from dead organisms. Ammonia may be utilised by organisms and converted to organic nitrogen compounds or oxidised bacterially to nitrite and thence to nitrate, which is the principal form in which combined nitrogen is stored in the sea.

In all earlier work, which has been reviewed by ROBINSON AND WIRTH[2], ammonia was determined by distillation with subsequent Nesslerisation. Later work has shown this procedure to yield high results on account of the decomposition of organic nitrogen compounds by the high alkalinity and elevated temperature employed during the distillation.

A number of workers have determined ammonia in sea water by means of the NESSLER method, modified to prevent the interference of magnesium salts, either by preliminary precipitation by means of barium chloride, sodium carbonate and sodium hydroxide[3,4,5,6] or by the use of tartrate as a complexing agent[7,8,9,10]. These methods, though rapid, lack precision owing to the colloidal nature and instability of the coloured product formed by the NESSLER reagent, and to the high alkalinity of the solution, which is liable to cause fission of any of the more labile nitrogen compounds, such as amides, etc., present in the water. HARVEY[1] reports that the NESSLER method lacks sufficient sensitivity for the determination of ammonia at concentrations of less than 10 mg/m^3.

KROGH[11] separated the ammonia from sea-water by vacuum distillation[12]. The ammonia was trapped in hydrobromic acid and determined titrimetrically using sodium hypobromite. KROGH claimed an accuracy of ± 0.04 μg of NH_4-N, corresponding to ± 2 mg NH_4-N/m^3. CONWAY[13] has determined ammonia in sea-water by micro-diffusion into hydrochloric acid, and titration of the excess acid with N/5,000 barium hydroxide. This method, though elegant, is unsuitable for the routine determination of ammonia in sea-water owing to the small volume of sample which can be used and to the delicacy of the titration technique.

In the course of a study of ammonia in sea-water a method was required for its routine determination which would be both quick and accurate. The NESSLER method was tried, but rejected on account of the impossibility of obtaining results better than ± 10%. It was concluded that the best approach would be the use of the KROGH vacuum distillation method, followed by a colorimetric method for the determination of the ammonia distilled.

A number of colorimetric methods have been described for the determination of ammonia in addition to the NESSLER method, principally, the pyridine-pyrazolone method[14], the hypobromite-naphthyl-red method[15], and a method based on the blue colour formed by the reaction of sodium phenate and sodium hypochlorite with ammonia. The last procedure seemed to offer the greatest prospect of having a sufficiently high sensitivity and of giving an accuracy of better than ± 1%.

The blue colour of indophenol formed by phenol and hypochlorite in the presence of ammonia was first reported by BERTHELOT[16] and was applied by THOMAS[17] to the determination of ammonia in biological fluids.

VAN SLYKE AND HILLER[18] determined ammonia in blood by treating the separated ammonia (removed by aeration of the sample) with solutions of sodium phenate in sodium hydroxide, and potassium hypochlorite. After heating to 100° for 3 minutes the intensity of the resultant blue colour was compared with standards. They claimed that 200 μg of NH_4-N/l could be readily detected. Their procedure with slight further modification has been used by several other workers[19,20,21] in biochemical and physiological investigations.

RUSSELL[22] was able to increase the sensitivity of the VAN SLYKE procedure threefold by the use of a sodium phenate reagent free from excess alkali and by the addition of a small amount of manganese salt as a catalyst. KIRK[23] has used the method for the determination of submicrogram amounts of ammonia with 10 μg as the lower practical limit. KULENOK[24] has recommended the phenol-hypochlorite reagent for water analysis in preference to NESSLER's reagent.

COLORIMETRIC DETERMINATION OF AMMONIA

Preliminary experiments, using the method of RUSSELL, gave very erratic results. These variable results were due to the difficulty of ensuring that all samples were heated at the same temperature for the same period of time. Experiments were made to determine the relation between intensity of colour and time of heating at various temperatures. They indicated that at 100° the full colour was attained in six minutes, but thereafter initially, fell off rapidly and then more slowly at about 15% per hour. At 70°, however, maximum colour was attained in *ca.* 35 minutes, and the colour (though slightly less intense than at 100°) remained constant for at least 1 hour. All subsequent work was carried out at a temperature of 70° with a heating period of 45 minutes.

Effect of variation of amounts of reagent

Sodium phenate. 15 ml portions of ammonium sulphate solution containing 2.5 µg NH_4-N/ml were treated with various amounts of sodium phenate reagent (containing 5.4 g sodium hydroxide, and 12.5 g of phenol per 100 ml), 2 ml of sodium hypochlorite reagent (containing 0.9% available chlorine), and 1 ml of 0.00024*M* manganese sulphate reagent, and then diluted to 25 ml. After heating at 70° for 45 minutes, the optical densities of the solution were measured in a 1 cm cell at 625 mµ. The results, which are shown in Table I, indicate that the colour intensity increases rapidly with increasing amount of phenate up to 3.7 ml and thereafter more gradually. It was decided, therefore, in order to keep the reagent blank as low as possible that 4 ml of sodium phenate solution should be employed in the determination.

TABLE I

EFFECT OF VARIATION OF VOLUME OF SODIUM PHENATE ON OPTICAL DENSITY OF SOLUTIONS

ml of sodium phenate	0.25	0.5	1	2	3	3.5	3.75	4	4.25	5	6	7
Determination*	0.053	0.081	0.143	0.244	0.328	0.361	0.370	0.394	0.397	0.409	0.422	0.429
Blank	—	0.003	—	0.010	—	—	—	0.016	—	0.018	—	0.021
Difference	0.052	0.078	0.137	0.234	0.315	0.347	0.355	0.378	0.381	0.391	0.402	0.408

* 37.5 µg NH_4-N/25 ml.

Sodium hypochlorite. Similar experiments were made using the same amount of ammonium sulphate solution, with 4 ml of sodium phenate reagent, and varying amounts of sodium hypochlorite reagent (containing 0.9 g available Cl per 100 ml), together with 1 ml of manganese sulphate reagent. The results, given in Table II, indicate that the optimum amount of hypochlorite is 2.0 ml and this volume of the reagent was used in all later work.

TABLE II

EFFECT OF VARIATION OF VOLUME OF SODIUM HYPOCHLORITE (0.9% AVAILABLE CHLORINE) ON OPTICAL DENSITY OF SOLUTIONS

ml of hypochlorite	0.1	0.25	0.5	0.75	1.0	1.25
Determination*	0.115	0.195	0.312	0.358	0.374	0.388
Blank	0.003	0.008	0.015	0.015	0.016	0.017
Difference	0.112	0.187	0.297	0.343	0.358	0.371
ml of hypochlorite	1.5	2	3	5		
Determination*	0.393	0.394	0.391	0.360		
Blank	0.017	0.017	0.016	0.017		
Difference	0.376	0.377	0.375	0.343		

* 37.5 μg NH_4-N/25 ml.

Manganese sulphate. In a similar manner the effect of the variation of the amount of manganese sulphate (0.00024*M*) was examined. The results are shown in Table III. They show that, as discovered by RUSSELL, the colour of the phenol-hypochlorite method is enhanced by *ca.* 30% in the presence of manganese, but that the reagent blank is also considerably increased. In all subsequent work 1 ml of manganese sulphate reagent was added.

TABLE III

EFFECT OF VARIATION OF VOLUME OF 0.00024*M* MANGANESE SULPHATE SOLUTION ON OPTICAL DENSITIES OF SOLUTIONS

ml of manganese sulphate	0	0.25	0.5	0.75	1.0
Determination*	0.296	0.322	0.378	0.391	0.398
Blank	0.007	0.012	0.017	0.019	0.020
Difference	0.289	0.310	0.361	0.372	0.378
ml of manganese sulphate	1.25	1.5	2	3**	
Determination*	0.400	0.402	0.407	0.434	
Blank	0.020	0.021	0.026	0.032	
Difference	0.380	0.381	0.381	0.402	

* 37.5 μg NH_4-N/25 ml.
** Precipitation of manganese hydroxide.

Fig. 1. shows the rate of colour development at various temperatures using the proposed conditions. At 70° maximum colour intensity is attained after 35 minutes and the colour remains constant for at least an hour thereafter. The principal difference between the proposed method and that of RUSSELL (apart from the lower temperature used for the colour development) is that twice as great a concentration of phenate and hypochlorite is used in the latter procedure.

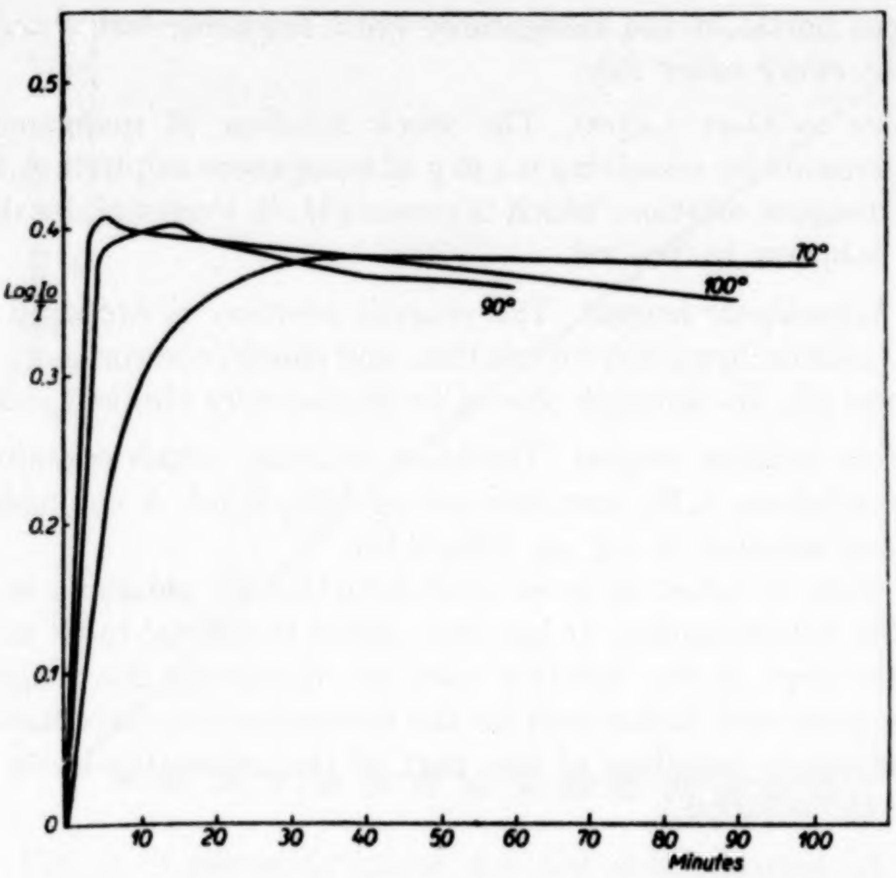

Fig. 1. Development of colour for various times at 100°, 90° or 70° using 37.5 μg NH_4-N (reagent blank deducted).

In addition, in the present work, the concentration of manganese has been reduced to a third of that used by RUSSELL, since the concentration which she employs is very close to the level at which precipitation of manganese salts occurs.

Method

All measurements of optical density were made with a Unicam S.P. 500 spectrophotometer, using a slit width of *ca.* 0.05 mm. pH measurements were made by means of a Cambridge Instruments pH meter, using a glass electrode.

Reagents

All reagents and solutions must be made up with water which has been freshly distilled from dilute sulphuric acid in an all-glass still.

1. *Sodium phenate reagent.* Dissolve 5.4 g of pure pellet sodium hydroxide in about 20 ml of water, boil for ½ minute and cool. Weigh out 12.5 g of phenol, B.P., into 100 ml graduated flask, and add to it 60 ml of water. Add the cold sodium hydroxide solution to the phenol and mix, while cooling under the tap. Make up to 100 ml with water. The reagent, which should be colourless, is preserved

in a dark glass bottle in the refrigerator until required, but should be made freshly at least every other day.

2. *Manganese sulphate reagent.* The stock solution of manganese sulphate ($0.008M$) is prepared by dissolving 0.446 g of manganese sulphate A.R. in 250 ml of water. The reagent solution, which is $0.00024M$, is prepared by diluting 3 ml of the stock solution to 100 ml.

3. *Sodium hypochlorite reagent.* The reagent solution is prepared by dilution of commercial sodium hypochlorite solution, and should contain 0.9 g of available chlorine per 100 ml. Its strength should be periodically checked iodometrically.

4. *Ammonium sulphate reagent.* The stock solution, which contains 0.4716 g/l of ammonium sulphate A.R., contains 100 μg NH_4-N/ml. A convenient dilution for the working solution is 2.5 μg NH_4-N/ml.

Great care must be taken to avoid contamination by ammonia or ammonium salts during the determination. It has been found beneficial to fit sulphuric acid bubblers to the tops of the burettes used for dispensing the reagents, and to steam out the graduated flasks used for the determination. Care should be taken to avoid unnecessary handling of any part of the apparatus likely to come in contact with the solution.

Determination

Place up to 15 ml of the test solution in a 25 ml glass stoppered graduated flask, and add to it 4 ml of the sodium phenate reagent; shake, and then add 2 ml of the hypochlorite solution, followed by 1 ml of the manganese sulphate solution, dilute to 25 ml with ammonia-free water. Mix well. Press home the glass stopper of the flask tightly, or replace it by a well fitting clean rubber bung. Heat the flask in a water bath at 70° for 45 minutes, cool, and after at least 10 minutes measure the optical density of the solution at 625 mμ. Run a blank determination using the reagent alone. Calibrate the method, using the ammonium sulphate solution.

Results

A calibration curve was prepared using known amounts of ammonium salt, it indicates (Fig. 2) that BEER's Law is obeyed up to a concentration of 2 mg NH_4-N/l. Above this concentration the change in optical density per unit weight of NH_4-N decreases; the reproducibility, however, remains good and the method may be used for the determination of concentrations of up to 6 mg NH_4-N/l, provided that the concentration is read from the calibration curve. The results obtained with 1-10 μg NH_4-N using 7.62 cm (3 inch) cells, and for 5-50 μg NH_4-N using 1 cm cells are shown in Tables IV and V respectively. They indicate that an overall standard deviation of 0.7% is obtained.

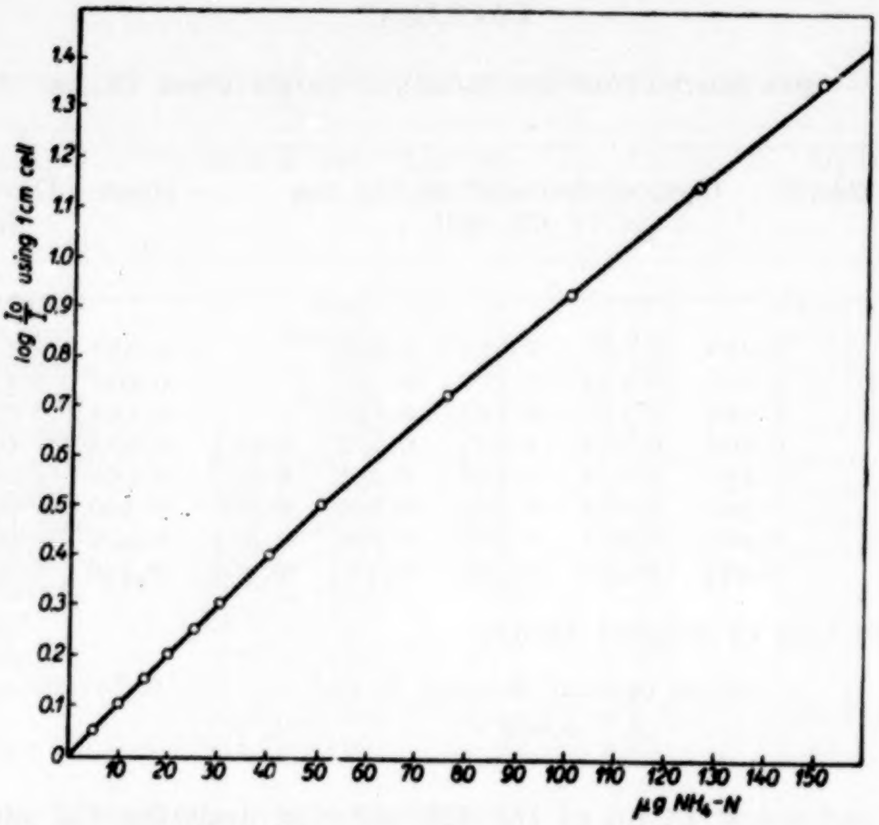

Fig. 2. Calibration curve for the determination of ammonia.

TABLE IV

DETERMINATION OF LOWER CONCENTRATIONS OF AMMONIA USING 7.62 cm (3 inch) CELLS

$\mu g\ NH_4$-N/25 ml	Optical density			mean	Deviation from linearity** %
1	0.074	0.076	0.078	0.076	0.5
2	0.156	0.152	0.152	0.153	0.2
3	0.227	0.226	0.229	0.228	0.5
4	0.305	0.307		0.306	0.2
5	0.386	0.386	0.379	0.382	0.3
10	0.767	0.767	0.769	0.768	0.5

* after deduction of reagent blank.

** $\mu g\ NH_4\text{-}N = \dfrac{\text{optical density}}{0.0764}$

Interference of foreign ions

The effect of various salts on the determination of ammonia was evaluated by adding to 15 ml of the salt solution in question, 40 μg NH_4-N. After development of the colour, the solution were measured at 625 mμ in 1 cm cells. Similar runs

TABLE V

DETERMINATION OF AMMONIA USING 1 cm CELLS

µg NH_4-N/25 ml	Optical density* at 625 mµ 1 cm cell					Mean	Deviation from linearity** %
5	0.050	0.051	0.051	0.051		0.051	+1.2
10	0.102	0.103	0.102	0.101		0.102	+1.2
15	0.152	0.152	0.151	0.151		0.152	+0.5
20	0.202	0.202	0.203	0.202	0.202	0.202	+0.2
25	0.251	0.251	0.252	0.251	0.253	0.252	±0.0
30	0.301	0.299	0.301	0.299	0.300	0.300	—0.8
40	0.401	0.401	0.402	0.399	0.403	0.401	—0.5
50	0.494	0.494	0.496	0.497	0.495	0.496	—1.5, mean 0.7 %

* after deduction of reagent blank.

$$** \ \mu g \ NH_4\text{-}N = \frac{\text{mean optical density} \times 10}{0.108}$$

were carried out using 15 ml of the salt solution omitting the addition of the ammonium salt. 40 µg NH_4-N gave an optical density of 0.401 with a reagent blank of 0.020. The results are shown in Table VI.

It will be seen that none of the ions normally present in natural fresh water will interfere with the determination of ammonia by the phenate-hypochlorite method. The procedure is not suitable, however, for the direct determination of ammonia in sea-water owing to the precipitation of magnesium hydroxide or phenate. Attempts to prevent the precipitation by means of tartrate or ethylenediaminetetra-acetic acid were not successful, since no blue colour was formed by ammonia in the presence of these reagents.

Ammonia may be determined in the presence of at least five hundred times its weight of hydrazine, since the latter is oxidised by hypochlorite directly to nitrogen. Hydroxylamine, on the other hand, yields a rather pale blue colour on the addition of sodium phenate reagent, which rapidly turns to the royal blue of the indophenol on addition of the hypochlorite.

Distillation of ammonia

To avoid the decomposition of unstable organic nitrogen compounds, the separation of ammonia from sea-water was carried out by distillation under reduced pressure from a faintly alkaline solution, using a gentle current of air to assist in the entrainment of the ammonia. The apparatus, which is shown in Fig. 3, is an all-glass modification of that employed by KROGH[11], and is electrically heated. It is evacuated by means of a filter pump to a pressure of 4-5 cm of mercury

TABLE VI

EFFECT OF FOREIGN IONS ON DETERMINATION OF AMMONIA

Substance	Added as	Concentration %	Optical density 40 μg NH_4-N	 Blank	 Difference
Sodium chloride	$NaCl$	1	0.422	0.033	0.389
Sodium sulphate	Na_2SO_4	1	0.411	0.023	0.388
Potassium chloride	KCl	1	0.428	0.039	0.389
Potassium nitrate	KNO_3	1	0.426	0.025	0.401
Potassium bromide	KBr	0.4	0.349	0.016	0.333
Magnesium chloride*	$MgCl_2.6H_2O$	0.2	0.370	0.016	0.354
Calcium chloride	$CaCl_2.6H_2O$	0.2	0.420	0.021	0.399
Strontium chloride	$SrCl_2.6H_2O$	0.2	0.389	0.026	0.363
Barium chloride	$BaCl_2.2H_2O$	0.2	0.374	0.016	0.358
Copper sulphate*	$CuSO_4.5H_2O$	0.05	0.201	0.043	0.158
Zinc sulphate*	$ZnSO_4.7H_2O$	0.05	0.317	0.016	0.301
Ferric chloride*	$FeCl_3.6H_2O$	0.05	0.392	0.017	0.375
Aluminium sulphate*	$Al_2(SO_4)_3.18H_2O$	0.05	0.433	0.025	0.408
Hydrazine	$N_2H_4.H_2SO_4$	0.01	0.419	0.021	0.398
Hydroxylamine	$NH_2OH.HCl$	0.01	2.88	2.48	0.400

* precipitate filtered off before measuring.

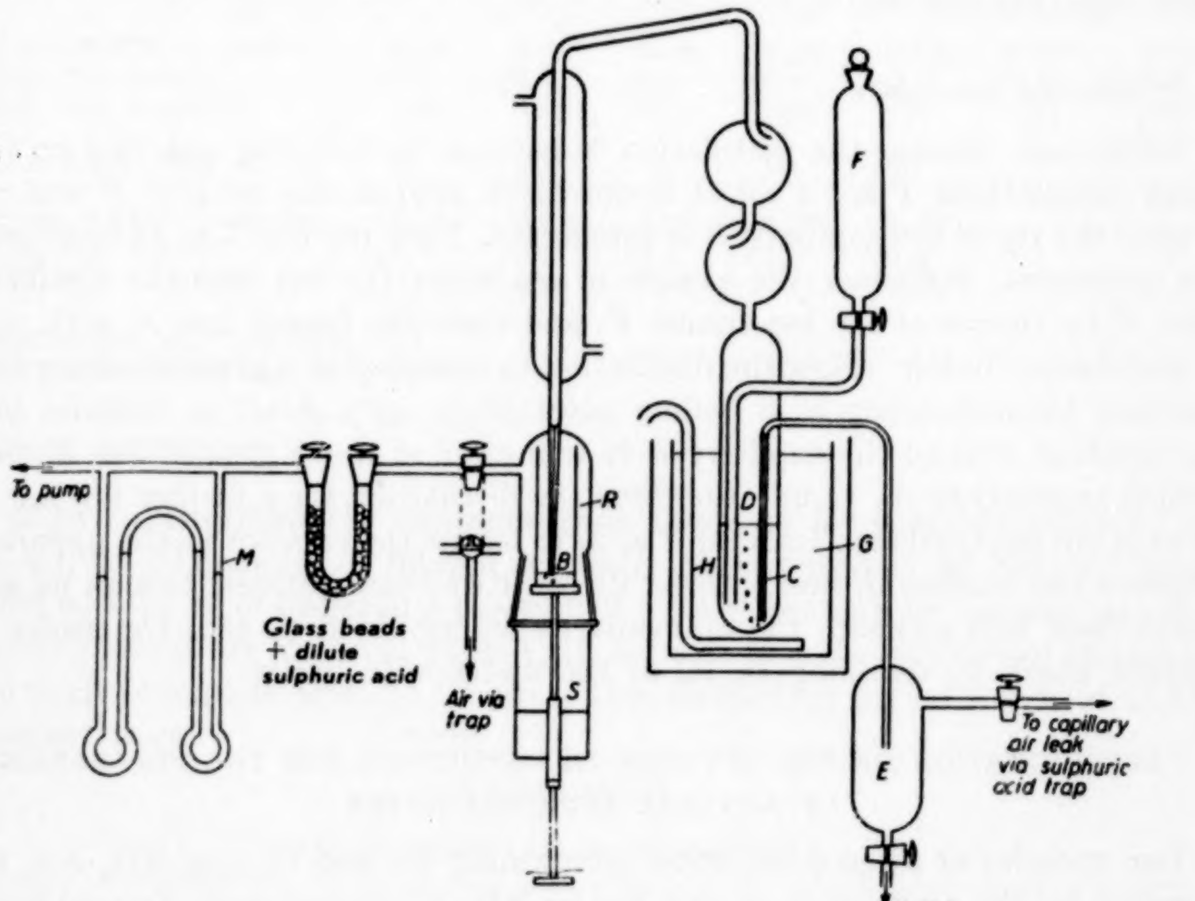
To pump
M
Glass beads
+ dilute
sulphuric acid
Air via
trap
R
B
S
F
D
H
C
G
E
To capillary
air leak
via sulphuric
acid trap
To sink

Fig. 3. Apparatus for the distillation of ammonia under reduced pressure.

(measured on the Manometer M). The distillation is carried out in the tube D, which is heated to 60° by means of the electrically heated water bath G. A gentle stream of acid washed air is admitted to D through the capillary C, and its flow is controlled by a capillary leak. After condensation, the distillate passes down the capillary B, which dips under the surface of 1 ml of *ca.* 0.01N hydrochloric acid contained in the receiver R; the latter may be raised or lowered by means of the coarse pitched screw S, working through a vacuum-tight gland packed with polyethylene. The tap T serves either to connect the apparatus to the filter pump, or to admit acid-washed air to the distillation train, thereby blowing the undistilled residue over into the trap E from which it can be drained away to the sink. To prevent contamination by traces of ammonia in the atmosphere, U-tubes containing glass beads and 2N sulphuric acid are fitted to all tubes leading into the apparatus.

Reagents

Metaborate buffer. Weigh 2.55 g of sodium metaborate into a 500 ml graduated flask, add 100 ml of 0.1N sodium-hydroxide, shake till dissolved and make up to the graduation with ammonia-free water.

Hydrochloric acid (0.01N). Dilute 1 ml of concentrated hydrochloric acid to 1 l with ammonia-free water.

Distillation procedure

Before use, cleanse the distillation apparatus by carrying out two or three blank distillations. Place 1 ml of hydrochloric acid in the receiver R and raise it until the tip of the capillary B is submerged. Turn the tap T so as to evacuate the apparatus. Introduce the sample of sea-water (50 ml) into the distillation tube D by means of the tap funnel F, and rinse the funnel into D with 10 ml of metaborate buffer Allow the distillation to continue at a pressure of 4-5 cm of mercury (corresponding to a boiling point of *ca.* 45°). After 10 minutes lower the receiver R until the capillary B is well clear of the surface of the distillate (which amounts to *ca.* 12 ml). Continue the distillation for a further few seconds to rinse out the capillary. Turn tap T so as to release the vacuum in the apparatus. Remove the receiver R and transfer its contents quantitatively to a 25 ml graduated flask and estimate the ammonia as described on p. 580. Determine the reagent blank by distilling 10 ml of the metaborate buffer.

DETERMINATION OF THE OPTIMUM PH CONDITIONS FOR THE SEPARATION OF AMMONIA FROM SEA-WATER

Two samples of filtered sea-water (containing 8.0 and 14.0 µg NH_4-N/l) were enriched by the addition of 40 and 800 µg NH_4-N/l respectively. Several buffers were prepared by mixing 25 ml of 0.1M sodium metaborate (10.19 g/l) with varied volumes of 0.1N sodium hydroxide or hydrochloric acid and diluting to 50 ml. Portions of 50 ml of the enriched sea-waters were treated with 10 ml of the buffers and distilled for 12 minutes at 5 cm pressure. The ammonia in the distillate was determined, giving the results shown in Table VII.

They indicated that complete recovery of ammonia from both samples of enriched sea-water with a distillation period of 12 minutes was only attainable at a pH of *ca.* 9.15. At higher pH values than this the recovery of ammonia drops off considerably perhaps owing to its partial retention by the precipitated magnesium salts which rapidly increase in amount as the alkalinity increases. Below pH 9.0 the recovery of ammonia decreases rapidly; but it is interesting to note that ammonia distils from sea-water at a pH of 7.8-8.2 — that of natural ocean water, suggesting that ammonia may be lost directly from the sea to the atmosphere.

TABLE VII

RECOVERY OF AMMONIA AT VARIOUS pH VALUES USING 10 ml OF METABORATE BUFFER. (25 ml 0.1M METABORATE + x ml OF 0.1N SODIUM HYDROXIDE OR z ml OF 0.1N HYDROCHLORIC ACID DILUTED TO 50 ml)

x ml of 0.1N NaOH	0	1	2.5	5	10	15	20
pH of sea-water + buffer	8.98	9.06	9.15	9.39	9.69	9.80	9.92
μg NH_4-N/l found*	46.6	46.9	47.5	46.0	42.0	39.6	38.0
μg NH_4-N/l found**	786	808	810	792	776	754	724
z ml of 0.1N HCl	1	2.5	5	10	20		
pH of sea-water + buffer	8.96	8.80	8.68	8.36	7.86		
μg NH_4-N/l found*	43.6	32.4	23.4	12.6	10.4		
μg NH_4-N/l found**	752	740	670	564	286		

* contained 48.0 μg NH_4-N/l.
** contained 814 μg NH_4-N/l.

Rate of distillation

In order to determine the minimum time necessary for complete recovery of ammonia, 50 ml samples of filtered sea-water containing 725 μg NH_4-N/l were distilled with 10 ml of buffer at a pressure of 4 cm of mercury for various periods. The results, which are shown in Table VIII, indicate that the recovery of ammonia is practically complete after 10 minutes. This distillation period was used in all subsequent work.

TABLE VIII

RATE OF DISTILLATION OF AMMONIA

Minutes	4	6	8	10	12
% recovery ammonia	83.4	91.5	96.1	99.5	99.6

Results

To test the reliability of the method for the estimation of ammonia in sea-water, duplicate determinations were carried out on a filtered sea-water which had been enriched with ammonium salt. The results are shown in Table IX.

TABLE IX

RECOVERY OF AMMONIA FROM 50 ml OF SEA-WATER

μg NH_4-N added	optical density		Mean	μg NH_4-N/l		Difference
				Found	Present	
Reagent blank	0.162	0.160	0.161	—	—	—
None	0.192	0.190	0.191	8.0	—	—
1	0.262	0.266	0.263	27.2	28.0	0.8
2	0.350	0.355	0.352	49.8	48.0	1.8
4	0.495	0.490	0.492	87.0	88.0	1.0
6	0.656	0.649	0.653	128.6	128.0	0.6
8	0.810	0.800	0.805	168.4	168.0	0.4

As a further test of the reproducibility of the distillation procedure several replicate determinations were carried out on samples of filtered sea-water. With ammonia concentrations of 7.1, 13.4 and 273.6* mg NH_4-N/m^3 the standard deviations were 0.7, 0.4 and 3.4 mg NH_4-N/m^3 respectively. It is considered that the accuracy of the method is limited by accidental contamination by ammonia. Better results might be achieved in laboratories situated away from industrial areas.

About 25 determinations of ammonia can be carried out per day if only one distillation train is employed; this number can be almost doubled if two stills are used concurrently.

It will be noted that the sea-water used in all the present work was filtered through a Whatman No. 2 paper to remove the larger particles of suspended organic matter. If these particles are not removed considerable variations may occasionally occur between replicate determinations owing perhaps to the release of ammonia adsorbed on their surfaces or to their partial decomposition[25].

Amino acids presumably occur in sea-water, formed by the hydrolysis of protein. To test whether they or urea interfere in either the direct colorimetric determination of ammonia or the vacuum distillation at pH 9.15, several B.D.H. amino acids, having a wide range of structures, were examined. The results, which are shown in Table X, indicate that in the colorimetric procedure only β-alanine causes any noticeable interference. None of the amino acids examined interferes appreciably when the ammonia is first separated by distillation.

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* Estuarine water probably contaminated with sewage.

TABLE X

INTERFERENCE OF AMINO ACIDS ON THE DETERMINATION OF AMMONIA

Acid	Not Distilled		Distilled	
	amino acid (mg)	NH_4-N found (µg)	amino acid (mg)	NH_4-N found (µg)
β-alanine	0.2	6.2	1.0	0.8
L-arginine HCl	0.1	0.6	0.3	0.6
DL-aspartic	0.2	0.6	1.0	0.2
L-glutamic	0.2	0.8	1.0	0.0
glycine	0.2	0.4	1.0	1.2
L-leucine	0.2	1.0	1.0	0.4
DL-methionine	0.2	0.2	1.0	0.2
DL-ornithine HBr	0.2	1.4	1.0	0.6
Urea	0.1	0.4	0.1	0.0
	0.2	0.0	1.0	0.0
	1.0	0.4		

ACKNOWLEDGEMENT

The Author wishes to thank Mr. JAMES MURPHY for his assistance in carrying out a number of the distillations in the later stages of the work.

SUMMARY

The conditions for the precise spectrophotometric determination of microgram amounts of ammonia by means of the sodium phenate-hypochlorite method of RUSSELL have been investigated. Several modifications of her procedure have been introduced, particularly in the time and temperature used for development of the blue colour. BEER's Law is obeyed up to a concentration of 2 mg NH_4-N/l. and ammonia can be determined with a standard deviation of 0.7%. The method can be used for the determination of up to at least 6 mg NH_4-N/l if recourse is made to a calibration curve. The interference of a number of inorganic ions has been studied, none of those which occur in natural fresh waters causes any marked diminution of the colour. The method can, therefore, be employed directly for the determination of ammonia in fresh waters. The most serious interferences are produced by copper and hydroxylamine. Hydrazine, however, does not interfere with the determination of ammonia unless it is present to the extent of at least 500 times the weight of the ammonia.

The phenate-hypochlorite method cannot be used for the direct estimation of ammonia in sea-water owing to the interference of magnesium and calcium ions. The ammonia is therefore separated from the sea-water by a preliminary distillation under reduced pressure in a slow current of air as suggested by KROGH. A metaborate buffer has been employed for the liberation of the ammonia, and the optimum conditions of alkalinity for its separation determined. If two distillation apparatus are used concurrently 40-50 samples of sea-water may be examined per day with a standard deviation of less than 1 mg NH_4-N/m^3.

Amino acids and urea do not interfere in either the sodium phenate-hypochlorite procedure or the distillation.

RÉSUMÉ

L'auteur étudie les conditions pour un dosage spectrophotométrique précis de traces d'ammoniac au moyen de la méthode de RUSSELL au phénate-hypochlorite

de sodium. Plusieurs modifications ont été faites, en particulier le temps et la température nécessaires au développement de la coloration bleue. La loi de Beer est vérifiée jusqu'à une concentration de 2 mg NH_4-N/l et l'ammoniac peut être déterminé avec une déviation de 0.7%. Cette méthode permet de doser jusqu'à au moins 6 mg a étudié aussi l'influence d'un certain nombre d'ions: les ions présents dans l'eau fraîche ne causent aucune diminution sensible de la coloration. Cette méthode peut donc être utilisée directement pour le dosage de NH_3 dans l'eau. Les plus sérieuses perturbations sont dues au cuivre et à l'hydroxylamine. L'hydrazine ne gêne pas pour des teneurs d'au moins 500 fois le poids de l'ammoniac. Cette méthode au phénate-hypochlorite ne peut pas être utilisée pour le dosage direct de NH_3 dans l'eau de mer, le magnésium et le calcium gênant la réaction. L'ammoniac est séparé de l'eau de mer par une distillation préliminaire sous pression réduite dans un faible courant d'air, comme proposé par Krogh. Un tampon au métaborate est utilisé pour libérer NH_3 et les conditions d'alcalinité sont étudiées. Si l'on utilise deux appareils à distiller, il est possible d'effectuer 40-50 dosages par jour avec un écart de moins de 1 mg NH_4-N/m^3. Les acides aminés et l'urée ne gênent pas, soit dans le procédé à l'hypochlorite-phénate de sodium, soit dans la distillation.

ZUSAMMENFASSUNG

Die Bedingungen für eine genaue spektrophotometrische Bestimmung von Mikromengen Ammoniak mit Hilfe der Natriumphenathypochloritmethode von Russell wurde untersucht. Meherer Abänderungen ihres Verfahrens wurden eingeführt, besonders bei der für die Entwicklung der blauen Farbe verwendeten Zeit und Temperatur. Das Beersche Gesetz wird bis zu einer Konzentration von 2 mg NH_4-N/l befolgt und Ammoniak kann mit einer geeichten Abweichung von 0.7% bestimmt werden. Die Methode kann für die Bestimmung von zumindest bis zu 6 mg NH_4-N/l benützt werden, wenn man eine Eichkurve als Hilfsmittel benützt. Eine Anzahl störender anorganischer Ionen wurde untersucht. Keine der in natürlichen frischen Wasser vorkommenden Ionen verursachen eine beträchtliche Verminderung der Farbe. Die Methode kann daher direkt zur Bestimmung von Ammoniak in frischem Wasser benützt werden. Am stärksten stören Kupfer und Hydroxylamin. Hydrazin jedoch stört die Bestimmung nicht, wenn es nicht in einer Menge von mindestens 500 × des Gewichts des Ammoniaks vorhanden ist.

Die Phenat-hypochloritmethode kann nicht zur direkten Bestimmung von Ammoniak in Seewasser wegen der störenden Magnesium- und Calciumionen verwendet werden. Ammoniak wird daher durch eine vorgehende Destillation unter verminderten Druck und Durchleiten eines schwachen Luftstroms, wie von Krogh vorgeschlagen wurde, aus dem Seewasser abgetrennt. Für die Freisetzung von Ammoniak wurde ein Metaboratpuffer verwendet und die optimalen Bedingungen der Alkalität für seine Abtrennung bestimmt. Bei der gleichzeitigen Verwendung von zwei Destillationsapparaturen können pro Tag 40-50 Seewasserproben geprüft werden mit einer geeichten Abweichung von weniger als 1 mg NH_4-N/m^3.

Aminosäuren und Harnstoff stören weder das Natriumphenat-hypochloritverfahren noch die Destillation.

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SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

ANALYTICAL ABSTRACTS

The Society of Public Analysts and Other Analytical Chemists has provided abstracts of the literature on analytical chemistry for readers of *The Analyst* ever since the journal was first published in 1876. For the last four years these abstracts were prepared by the Bureau of Abstracts and supplied to members of the Society and to subscribers to *The Analyst* under the title *British Abstracts C*. The Bureau of Abstracts will cease to exist at the end of 1953, and British Abstracts will not appear in their present form thereafter.

In these circumstances, the Council of the Society has decided to resume publication of abstracts of analytical literature. *British Abstracts C* will be replaced in the new year by a new publication to be called *Analytical Abstracts*. This will be edited by Norman Evers, B.Sc., Ph.D., F.R.I.C., and published by W. Heffer & Sons Ltd. for the Society, and it will cover the whole range of analytical literature in the same way as did *British Abstracts C*. It is expected that it will be possible to extend its usefulness to readers as time passes.

Analytical Abstracts will appear each month bound separately from *The Analyst* and in a format similar to that of the abstracts included in *The Analyst* prior to 1950. The two journals, *The Analyst* and *Analytical Abstracts* will be available in 1954 to members of the Society and to subscribers on the same terms as obtained for *The Analyst* and *British Abstracts C* in 1953, or sold separately at 50*s*. per annum, including the index, or at 60*s*. per annum, printed on one side only, without the index.

Special arrangements are being made for members of kindred societies to obtain *Analytical Abstracts*.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the Society

An Ordinary Meeting of the Society (organised by the Physical Methods Group) was held at 5 p.m. on Friday, October 23rd, 1953, in the Lecture Hall, Southampton University. The Chair was taken by the President, Dr. D. W. KENT-JONES, F.R.I.C.

The subject of the meeting was *Paper Electrophoresis* and the following papers were presented and discussed: —

The Analysis of Inorganic Compounds by Electromigration and Electrochromatography, by F. H. POLLARD, B.Sc., Ph.D.

The subject was introduced by reference to early experiments of O. LODGE and J. KENDALL, and the conditions affecting electromigration and the types of cells used for inorganic separations were described. Examples of separation achieved on (a) paper and (b) in agar jelly were given. The effect of complex-forming agents and the use of columns was described.

The combination of electromigration with solvent flow chromatography was described. The types of cell used for discontinuous and continuous separations, the principles involved in continuous and discontinuous procedures, and examples of the separations attained by such processes were given. One-way, two-way and three-way separations and the use of complex-forming reagents were described.

The methods have been applied to the separation of rare earths and radioactive elements from other inorganic material.

The use of ion-exchange resins in electromigration was also described.

The Use of Paper Electrophoresis in the Study of Nucleic Acids, by ROY MARKHAM, M.A., Ph.D.

The degradation products of nucleic acids produced by chemical or enzymatic hydrolysis are extremely difficult substances to separate by chromatographic methods. This is largely because they occur as families of compounds having very similar structures and differing only in their purine and pyrimidine composition. Fortunately, these bases contain specific ionising groups, and by taking advantage of their differing pK values it is possible to effect the separation of the various compounds by electrophoresis on paper.

Although to some extent empirical, the method has the great advantage that predictions as to the relative rates of movement of various compounds can be made with some confidence, and conversely the method can be used to detect the presence or absence of certain groupings in the molecules by the use of very small amounts of material. This is analogous to electrometric titration, which requires many times the quantity of the substance.

Besides its purely analytical use, the paper electrophoresis method can be used in the preparation of reasonably large amounts of pure materials, and by the use of high voltage gradients, combined with adequate cooling, such separations can be carried out in one to three hours.

The design of an inexpensive high-voltage paper electrophoresis apparatus was described.

Paper-Strip Electrophoresis of Serum Proteins, by A. L. LATNER, M.Sc., M.D., F.R.I.C.

The apparatus and technique for paper-strip electrophoresis was briefly described. A brief account was also given of the methods of staining and scanning used by the author, including a simple visual method of scanning. The procedure has proved quantitative and evidence for this was given. The method cannot be strictly compared with the classical Tiselius procedure on serum. This also estimates lipoid material in combination with proteins which does not affect the paper-strip method.

Results obtained with the sera of different animals were discussed, since interesting differences between species have been observed. Some applications of the technique to problems of human disease were also given.

The meeting was preceded by an afternoon visit to the Esso Refinery at Fawley.

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, November 4th, 1953, in the Meeting Room of the Chemical Society, Burlington House, London W.1. The Chair was taken by the President, Dr. D. W. KENT-JONES, F.R.I.C., and over 80 members and visitors, including members of the Iron and Steel Institute, the Institution of Mining and Metallurgy, the British Iron and Steel Research Association and the British Non-Ferrous Metals Research Association, were present.

The subject of the meeting was *The Determination of Niobium in Minerals and Mineral Dressing Products* and the following papers were presented:

The Absorptiometric Determination of Niobium in Some African Low-grade Minerals and Mineral Dressing Products, by G. W. C. MILNER, B. Sc., R.F.I.C., A. Inst. P., AND A. A. SMALES, B. Sc., F.R.I.C.

A method was described for the determination of between 0.05 per cent. and 16 per cent. of niobium pentoxide in head samples and mineral dressing fractions produced during treatment of Sukulu soils (mainly magnetite, apatite, and quartz) and Nigerian granite (mainly quartz and cryolite). After chemical attack on the sample, the niobium is separated from the bulk of the other materials by precipitation with tannic acid and cinchonine with silica as carrier, and is finally determined absorptiometrically with potassium thiocyanate. The separation steps need not be quantitative because radiometric correction for losses is made by incorporating niobium-95 tracer in the procedure.

The Absorptiometric Determination of Niobium in Some African Low-grade Ores, by A. E. O. MARZYS, B. Sc., A.R.I.C.

The absorption of light in a region near to the ultra violet by the reduced niobium-thiocyanate complex in an organic medium is made a basis for the determination of niobium in low-grade ores and minerals. The respective merits of a mixture of acid acetone and of ether extract as a solvent were described. The method has been adapted for use with a Spekker absorptiometer provided with a mercury vapour lamp. Four modifications of the main procedure were described for use in the presence of certain interfering elements.

Results for a variety of African soils and minerals were compared with those obtained by gravimetric methods. The precision of the method is as good as, and probably better than, that of gravimetric methods when applied to complex soils and rocks of low niobium content. The speed and ease of manipulation are greatly increased.

By suitable adjustment of the amounts of material used, the method can be extended to all niobium minerals. The ratio of niobium to tantalum in mixed oxides can be rapidly found by determining niobium and titanium colorimetrically and calculating the tantalum content by difference.

Spectrographic Determination of Niobium and Tantalum in Sukulu-type Soils, by C. S. CAMPBELL, M.A., AND D. NICHOLAS.

A solution method for the spectrographic determination of niobium and tantalum in a low-grade ore was described. After an initial hydrochloric acid extraction, the sample residue is taken up in hydrofluoric acid. Molybdenum is added as internal standard and the solution is fed into a condensed arc discharge from a porous cup electrode. The lines Nb 2698 A and Mo 2688 A give a standard deviation of about 2 per cent.; tantalum is present in much smaller concentration and is estimated visually by using the line Ta 2685 A.

Inorganic Chromatography on Cellulose. Part XIV. A Shortened Method for the Determination of Niobium and Tantalum in Minerals and Ores, by R. A. MERCER AND R. A. WELLS, B. Sc., A.R.I.C.

A chromatographic procedure for the extraction of the mixed oxides of tantalum and niobium from minerals and ores was described. A solution of the sample in hydrofluoric acid containing ammonium fluoride is absorbed on cellulose and transferred to a 3-inch column of cellulose. Complete extraction of the niobium and tantalum is attained by passing 400 ml of methyl ethyl ketone, containing 15 per cent. v/v of 40 per cent. hydrofluoric acid, through the column. The separation is complete from all metals other than tungsten. The two oxides, recovered from this solvent, are subsequently separated by further chromatography or estimated without separation by a suitable colorimetric procedure.

The Colorimetric Estimation of Niobium and Tantalum with Pyrogallol, by E. C. HUNT, B.Sc., A.R.I.C., AND R. A. WELLS, B. Sc., A.R.I.C.

Colorimetric procedures for the estimation of niobium and tantalum in mixtures of the oxides of two metals were described. The method is applied to the estimation of the two metals in mixtures obtained by their chromatographic extraction from minerals and ores. The determinations are based upon the coloured complex formed between tantalum and pyrogallol in acid solution and between niobium and pyrogallol in alkaline solution. Both systems obey BEER's law and, with 1-cm cells, the optimum limits of concentration are 0 to 20 p.p.m. for niobium and 0 to 80 p.p.m. for tantalum. The effect of variation in pH and the interference of a number of cations and anions is recorded.

Inorganic Chromatography on Cellulose. Part XV. A Rapid Method for the Determination of Niobium in Low-grade Ores, by E. C. HUNT, B. Sc., A.R.I.C., AND R. A. WELLS, B.Sc., A.R.I.C.

A rapid and simple method was described for the determination of niobium in a hydrofluoric acid solution of an ore; it makes use of upward diffusion on a paper strip. The niobium is detected as a yellow band by spraying the strip with tannic acid. An accurate estimation of niobium can be made by direct visual comparison of the band with standard strips. Alternatively, a simple densitometer, which was described, permits a direct estimation to be made of the niobium on the strip. The chromatographic separation takes 20 minutes, and a simple technique for running 10 separations simultaneously was described. An accuracy of 10 per cent. is attained for ores containing 0.16 to 0.6 per cent of Nb_2O_5.

Contributions to the discussion following the papers were made by Mr. E. A. HONTOIR, Rio Tinto Co. Ltd.; Mr. L. E. GARDNER, B.I.S.R.A.; Mr. W. RAMSDEN, British Non-Ferrous Metals Res. Assoc.; Mr. A. BOWES AND Mr. T. BURCHELL, Murex Ltd.; Mr. A. R. POWELL, Johnson, Matthey & Co. Ltd.; Mr. W. H. BENNETT, Colonial Geological Surveys; Mr. B. BAGSHAWE, Brown-Firth Laboratories.